
CHAPTER 9

VISCOSITY

9-1 Scope

The first part of this chapter deals with the viscosity of gases and the second with the viscosity of liquids. In each part, methods are recommended for: (1) correlating viscosities with temperature; (2) estimating viscosities when no experimental data are available; (3) estimating the effect of pressure on viscosity; and (4) estimating the viscosities of mixtures. The molecular theory of viscosity is considered briefly.

9-2 Definitions of Units of Viscosity

If a shearing stress is applied to any portion of a confined fluid, the fluid will move with a velocity gradient with its maximum velocity at the point where the stress is applied. If the local shear stress per unit area at any point is divided by the velocity gradient, the ratio obtained is defined as the viscosity of the medium. Thus, viscosity is a measure of the internal fluid friction, which tends to oppose any dynamic change in the fluid motion. An applied shearing force will result in a large velocity gradient at low viscosity. Increased viscosity causes each fluid layer to exert a larger frictional drag on adjacent layers which in turn decreases the velocity gradient.

It is to be noted that viscosity differs in one important respect from the properties discussed previously in this book; namely, viscosity can only be measured in a nonequilibrium experiment. This is unlike density which can be found in a static apparatus and so is an equilibrium property. On the microscale, however, both properties reflect the effects of molecular motion and interaction. Thus, even though viscosity is ordinarily referred to as a nonequilibrium property; it is, like density, a function of the thermodynamic state of the fluid; in fact, it may even be used to define the state of the material. Brulé and Starling (1984) have emphasized the desirability of using both viscosity and thermodynamic data to characterize complex fluids and to develop correlations. This discussion is limited to Newtonian fluids, i.e., fluids in which the viscosity, as defined, is independent of either the magnitude of the shearing stress or velocity gradient (rate of shear). For polymer solutions which are non-Newtonian, the reader is referred to Ferry (1980) or Larson (1999).

The mechanisms and molecular theory of gas viscosity have been reasonably well clarified by nonequilibrium statistical mechanics and the kinetic theory of gases (Millat, et al., 1996), but the theory of liquid viscosity is less well developed. Brief summaries of both theories will be presented.

Since viscosity is defined as a shearing stress per unit area divided by a velocity gradient, it should have the dimensions of (force) (time)/(length)² or mass/(length) (time). Both dimensional groups are used, although for most scientific work, viscosities are expressed in poises, centipoises, micropoises, etc. A poise (P) denotes a viscosity of 0.1 N · s/m² and 1.0 cP = 0.01 P. The following conversion factors apply to viscosity units:

$$1 \text{ P} = 100 \text{ cP} = 1.000 \times 10^6 \mu\text{P} = 0.1 \text{ N s/m}^2 = 1 \text{ g/(cm} \cdot \text{s)} = 0.1 \text{ Pa} \cdot \text{s} \\ = 6.72 \times 10^{-2} \text{ lb-mass/(ft} \cdot \text{s)} = 242 \text{ lb-mass/(ft} \cdot \text{h)}$$

$$1 \text{ cP} = 1 \text{ mPa} \cdot \text{s}$$

The *kinematic viscosity* is the ratio of the viscosity to the density. With viscosity in poises and the density of grams per cubic centimeter, the unit of kinematic viscosity is the *stoke*, with the units square centimeters per second. In the SI system of units, viscosities are expressed in N · s/m² (or Pa · s) and kinematic viscosities in either m²/s or cm²/s.

9-3 Theory of Gas Transport Properties

The theory of gas transport properties is simply stated, but it is quite complex to express in equations that can be used directly to calculate viscosities. In simple terms, when a gas undergoes a shearing stress so that there is some bulk motion, the molecules at any one point have the bulk velocity vector added to their own random velocity vector. Molecular collisions cause an interchange of momentum throughout the fluid, and this bulk motion velocity (or momentum) becomes distributed. Near the source of the applied stress, the bulk velocity vector is high, but as the molecules move away from the source, they are “slowed down” due to random molecular collisions. This random, molecular momentum interchange is the predominant cause of gaseous viscosity.

Elementary Kinetic Theory

If the gas is modeled in the simplest manner, it is possible to show the general relations among viscosity, temperature, pressure, and molecular size. More rigorous treatments yield similar relations but with important correction factors. The elementary gas model assumes all molecules to be nonattracting rigid spheres of diameter σ (with mass m) moving randomly at a mean velocity v . The molar density is n molecules in a unit volume while the mass density is the mass in a unit volume. Molecules move in the gas and collide transferring momentum in a velocity gradient and energy in a temperature gradient. The motion also transfers molecular species in a concentration gradient. The net flux of momentum, energy, or component mass between two layers is assumed proportional to the momentum, energy, or mass density gradient, i.e.,

$$\text{Flux} \propto -\frac{d\rho'}{dz} \quad (9-3.1)$$

where the density ρ' decreases in the $+z$ direction and ρ' may be ρ_i (mass density),

nmv_y , (momentum density), or $C_v nT$ (energy density). The coefficient of proportionality for all these fluxes is given by elementary kinetic theory as $vL/3$, where v is the average molecular speed and L is the mean free path.

Equation (9-3.1) is also used to define the transport coefficients of diffusivity D , viscosity η , and thermal conductivity λ ; that is,

$$\text{Mass flux} = -Dm \frac{dn_i}{dz} = -\frac{vL}{3} \frac{d\rho_i}{dz} \quad (9-3.2)$$

$$\text{Momentum flux} = -\eta \frac{dv_y}{dz} = -\frac{vL}{3} mn \frac{dv_y}{dz} \quad (9-3.3)$$

$$\text{Energy flux} = -\lambda \frac{dT}{dz} = -\frac{vL}{3} C_v n \frac{dT}{dz} \quad (9-3.4)$$

Equations (9-3.2) to (9-3.4) define the transport coefficients D , η , and λ . If the average speed is proportional to $(RT/M)^{1/2}$ and the mean free path to $(n\sigma^2)^{-1}$,

$$D = \frac{vL}{3} = (\text{const}) \frac{T^{3/2}}{M^{1/2} P \sigma^2} \quad (9-3.5)$$

$$\eta = \frac{mpvL}{3} = (\text{const}) \frac{T^{1/2} M^{1/2}}{\sigma^2} \quad (9-3.6)$$

$$\lambda = \frac{vL C_v n}{3} = (\text{const}) \frac{T^{1/2}}{M^{1/2} \sigma^2} \quad (9-3.7)$$

The constant multipliers in Eqs. (9-3.5) to (9-3.7) are different in each case; the interesting fact to note from these results is the dependency of the various transfer coefficients on T , P , M , and σ . A similar treatment for rigid, nonattracting spheres having a Maxwellian velocity distribution yields the same final equations but with slightly different numerical constants.

The viscosity relation [Eq. (9-3.6)] for a rigid, non-attracting sphere model is (see page 14 of Hirschfelder, et al., 1954)

$$\eta = 26.69 \frac{(MT)^{1/2}}{\sigma^2} \quad (9-3.8)$$

where η = viscosity, μP
 M = molecular weight, g/mol
 T = temperature, K
 σ = hard-sphere diameter, Å

Analogous equations for λ and D are given in Chaps. 10 and 11.

Effect of Intermolecular Forces

If the molecules attract or repel one another by virtue of intermolecular forces, the theory of Chapman and Enskog is normally employed (Chapman and Cowling, 1939; Hirschfelder, et al., 1954). There are four important assumptions in this development: (1) the gas is sufficiently dilute for only binary collisions to occur (ideal

gas); (2) the motion of the molecules during a collision can be described by classical mechanics; (3) only elastic collisions occur, and (4) the intermolecular forces act only between fixed centers of the molecules; i.e., the intermolecular potential function is spherically symmetric. With these restrictions, it would appear that the resulting theory should be applicable only to low-pressure, high-temperature monatomic gases. The pressure and temperature restrictions are valid for polyatomic gases and, except for thermal conductivity (See Chap. 10) are adequate for most modeling purposes.

The Chapman-Enskog treatment develops integral relations for the transport properties when the interactions between colliding molecules are described by a potential energy function $\psi(r)$. The equations require complex numerical solution for each choice of intermolecular potential model. In general terms, the first-order solution for viscosity can be written

$$\eta = \frac{(26.69)(MT)^{1/2}}{\sigma^2 \Omega_v} \quad (9-3.9)$$

where the temperature dependence of the collision integral, Ω_v is different for each $\psi(r)$ and all symbols and units are as defined in Eq. (9-3.8). Ω_v is unity if the molecules do not attract each other. Corrections can be found in Chapman and Cowling (1939) and Hirschfelder, et al. (1954). The use of Ω_v from the Lennard-Jones (12-6) potential function is illustrated in Sec. 9-4.

9-4 ESTIMATION OF LOW-PRESSURE GAS VISCOSITY

Essentially all gas viscosity estimation techniques are based on either the Chapman-Enskog theory or the law of corresponding states. Both approaches are discussed below, and recommendations are presented at the end of the section. Experimental values of low-pressure gas viscosities are compiled in Landolt-Bornstein (1955), Stephan and Lucas (1979), and Vargaftik, et al. (1996). Literature references for a number of substances along with equations with which to calculate gas viscosities based on critically evaluated data may be found in Daubert, et al. (1997). Gas phase viscosity information can also be found in Dean (1999), Lide (1999), Perry and Green (1997), and Yaws (1995, 1995a). This information should be used with caution in those cases where constants in equations have been determined from estimated rather than experimental viscosities.

Theoretical Approach

The first-order Chapman-Enskog viscosity equation was given as Eq. (9-3.9). To use this relation to estimate viscosities, the collision diameter σ and the collision integral Ω_v must be found. In the derivation of Eq. (9-3.9), Ω_v is obtained as a function of a dimensionless temperature T^* which depends upon the intermolecular potential chosen. For any potential curve, the dimensionless temperature T^* is related to ε by

$$T^* = \frac{kT}{\varepsilon} \quad (9-4.1)$$

where k is Boltzmann's constant and ε is the minimum of the pair-potential energy. The working equation for η must have as many parameters as were used to define the original $\psi(r)$ relation. While many potential models have been proposed (Hirschfelder, et al., 1954), the Lennard-Jones 12-6 was the first and has most often been applied for ideal gas viscosity.

$$\psi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (9-4.2)$$

In Eq. (9-4.2), σ is like a molecular diameter and is the value of r that causes $\psi(r)$ to be zero. With this potential, the collision integral has been determined by a number of investigators (Barker, et al., 1964; Hirschfelder, et al., 1954; Itan, et al., 1961; Klein and Smith, 1968; Monchick and Mason, 1961; and O'Connell and Prausnitz, 1965). Neufeld, et al. (1972) proposed an empirical equation which is convenient for computer application:

$$\Omega_v = [A(T^*)^{-B}] + C[\exp(-DT^*)] + E[\exp(-FT^*)] \quad (9-4.3)$$

where $T^* = kT/\varepsilon$, $A = 1.16145$, $B = 0.14874$, $C = 0.52487$, $D = 0.77320$, $E = 2.16178$, and $F = 2.43787$. Equation (9-4.3) is applicable from $0.3 \leq T^* \leq 100$ with an average deviation of only 0.064%. A graph of $\log \Omega_v$ as a function of $\log T^*$ is shown in Fig. 9-1.

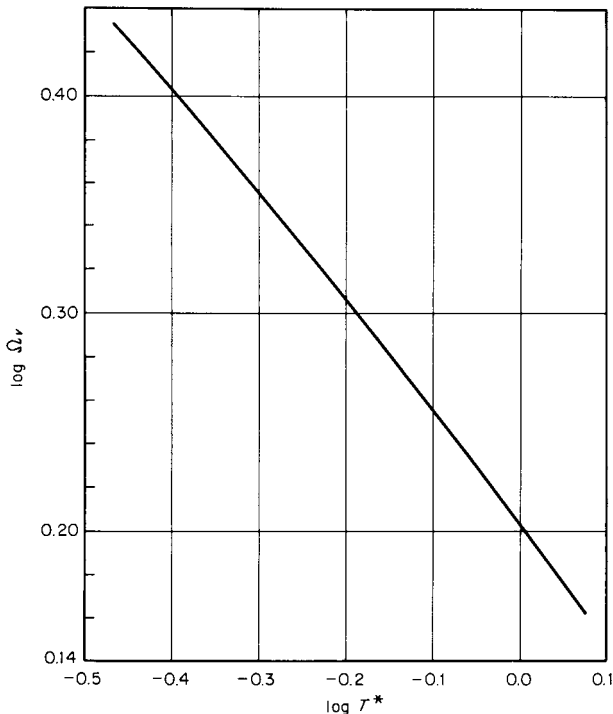


FIGURE 9-1 Effect of temperature on the Lennard-Jones viscosity collision integral.

With values of Ω_v as a function of T^* , a number of investigators have used Eq. (9-3.9) and regressed experimental viscosity-temperature data to find the best values of ε/k and σ for many substances. Appendix B lists a number of such sets as reported by Svehla (1962). It should be noted, however, that there appears also to be a number of other quite satisfactory *sets* of ε/k and σ for any given compound. For example, with *n*-butane, Svehla suggested $\varepsilon/k = 513.4$ K, $\sigma = 4.730$ Å, whereas Flynn and Thodos (1962) recommend $\varepsilon/k = 208$ K and $\sigma = 5.869$ Å.

Both sets, when used to calculate viscosities, yield almost exactly the same values of viscosity as shown in Fig. 9-2. This interesting paradox has been resolved by Reichenberg (1971), who suggested that $\log \Omega_v$ is essentially a linear function of $\log T^*$ (see Fig. 9-1).

$$\Omega_v = a (T^*)^n \quad (9-4.4)$$

Kim and Ross (1967) do, in fact, propose that:

$$\Omega_v = 1.604 (T^*)^{-0.5} \quad (9-4.5)$$

where $0.4 \leq T^* \leq 1.4$. They note a maximum error of only 0.7%. Substitution of Eq. (9-4.5) into Eq. (9-3.9) leads to

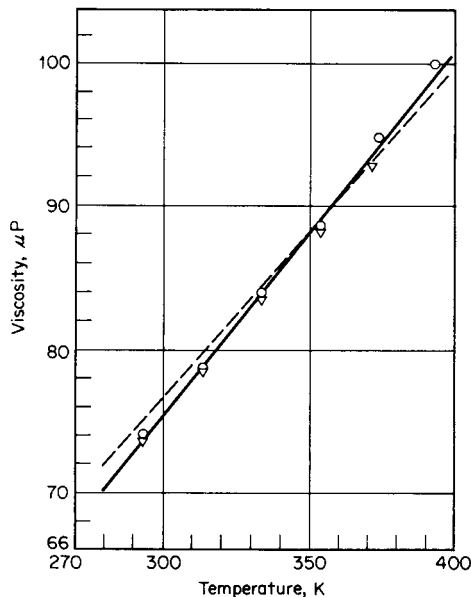


FIGURE 9-2 Comparison of calculated and experimental low-pressure gas viscosity of *n*-butane with Eq. (9-3.9) and the Lennard-Jones Potential: --- Flynn and Thodos (1962) with $\sigma = 5.869$ Å and $\varepsilon/k = 208$ K. — Svehla (1962) with $\sigma = 4.730$ Å and $\varepsilon/k = 513.4$ K. o (Titani, 1929); ▽ (Wobster and Mueller, 1941).

$$\eta = \frac{16.64(M)^{1/2}T}{(\varepsilon/k)^{1/2}\sigma^2} \quad (9-4.6)$$

where the units are the same as in Eq. (9-3.9). Here the parameters σ and ε/k are combined as a *single* term $(\varepsilon/k)^{1/2}\sigma^2$. There is then no way of delineating individual values of ε/k and σ by using experimental viscosity data, at least over the range where Eq. (9-4.5) applies. Equation (9-4.6) suggests that when $T_r \leq 1.4$, low-pressure gas viscosities are essentially proportional to the absolute temperature.

The conclusion to be drawn from this discussion is that Eq. (9-3.9) can be used to calculate gas viscosity, although the chosen set of ε/k and σ may have little relation to molecular properties. There will be an infinite number of acceptable sets as long as the temperature range is not too broad, e.g., if one limits the estimation to the range of reduced temperatures from about 0.3 to 1.2. In using published values of ε/k and σ for a fluid of interest, the two values from the same set must be used—never ε/k from one set and σ from another.

The difficulty in obtaining a priori meaningful values of ε/k and σ has led most authors to specify rules which relate ε/k and σ to macroscopic parameters such as the critical constants. One such method is shown below.

Method of Chung, et al. (1984, 1988)

These authors have employed Eq. (9-3.9) with

$$\frac{\varepsilon}{k} = \frac{T_c}{1.2593} \quad (9-4.7)$$

$$\sigma = 0.809V_c^{1/3} \quad (9-4.8)$$

where ε/k and T_c are in kelvins, σ is in angstroms, and V_c is in cm^3/mol . Then, using Eqs. (9-4.1) and (9-4.7),

$$T^* = 1.2593T_r \quad (9-4.9)$$

Ω_v in Eq. (9-3.9) is found from Eq. (9-4.3) with T^* defined by Eq. (9-4.9). Chung, et al. also multiply the right-hand side of Eq. (9-3.9) by a factor F_c to account for molecular shapes and polarities of dilute gases. Their final result may be expressed as:

$$\eta = 40.785 \frac{F_c(MT)^{1/2}}{V_c^{2/3}\Omega_v} \quad (9-4.10)$$

where η = viscosity, μP

M = molecular weight, g/mol

T = temperature, K

V_c = critical volume, cm^3/mol

Ω_v = viscosity collision integral from Eq. (9-4.3) and $T^* = 1.2593T_r$

$$F_c = 1 - 0.2756\omega + 0.059035 \mu_r^4 + \kappa \quad (9-4.11)$$

In Eq. (9-4.11), ω is the acentric factor (See Chap. 2) and κ is a special correction for highly polar substances such as alcohols and acids. Values of κ for a few such materials are shown in Table 9-1. Chung, et al. (1984) suggest that for other al-

TABLE 9-1 The Association Factor κ in Eq. (9-4.11) (Chung, et al., 1988)

Compound	κ	Compound	κ
Methanol	0.215	<i>n</i> -Pentanol	0.122
Ethanol	0.175	<i>n</i> -Hexanol	0.114
<i>n</i> -Propanol	0.143	<i>n</i> -Heptanol	0.109
<i>i</i> -Propanol	0.143	Acetic Acid	0.0916
<i>n</i> -Butanol	0.132	Water	0.076
<i>i</i> -Butanol	0.132		

cohols not shown in Table 9-1, $\kappa = 0.0682 + 4.704[(\text{number of } -\text{OH groups})/\text{molecular weight}]$. The term μ_r is a dimensionless dipole moment. (See discussion in Chap. 2 and also under Eq. (9-4.17) for techniques to nondimensionalize a dipole moment.) When V_c is in cm^3/mole , T_c is in kelvins, and μ is in debyes,

$$\mu_r = 131.3 \frac{\mu}{(V_c T_c)^{1/2}} \quad (9-4.12)$$

Example 9-1 Estimate the viscosity of sulfur dioxide gas at atmospheric pressure and 300°C by using the Chung, et al. method. The experimental viscosity is 246 μP (Landolt-Bornstein, 1955).

solution From Appendix A, $T_c = 430.8 \text{ K}$, $V_c = 122 \text{ cm}^3/\text{mole}$, $M = 64.065$, and the dipole moment is 1.6 debyes. From Eq. (2-3.3), $\omega = 0.257$. Assume κ is negligible. From Eq. (9-4.12),

$$\mu_r = \frac{(131.3)(1.6)}{[(122)(430.8)]^{1/2}} = 0.916$$

and with Eq. (9-4.11),

$$F_c = 1 - (0.2756)(0.257) + (0.059035)(0.916)^4 = 0.971$$

$$T^* = 1.2593 \frac{300 + 273}{430.8} = 1.675$$

Then, with Eq. (9-4.3), $\Omega_v = 1.256$. The viscosity is determined from Eq. (9-4.10).

$$\eta = (40.785)(0.971) \frac{[(64.065)(300 + 273)]^{1/2}}{(122)^{2/3}(1.256)} = 245.5 \mu \text{ P}$$

$$\text{Error} = \frac{245.5 - 246}{246} \times 100 = -0.2\%$$

Experimental viscosities and those estimated by the Chung, et al. method are shown in Table 9-2. The critical properties used to prepare Table 9-2 differed slightly from those in Appendix A. The average absolute error was about 1.9%. This agrees well with the more extensive comparison by Chung (1980), who found an average absolute error of about 1.5%.

Corresponding States Methods

From an equation such as (9-3.9), if one associates σ^3 with V_c [as in Eq. (9-4.8)] and assumes V_c is proportional to RT_c/P_c , a dimensionless viscosity can be defined:

$$\eta_r = \xi \eta = f(T_r) \quad (9-4.13)$$

$$\xi = \left[\frac{(RT_c)(N_o)^2}{M^3 P_c^4} \right]^{1/6} \quad (9-4.14)$$

In SI units, if $R = 8314 \text{ J/(kmol} \cdot \text{K)}$ and N_o (Avogadro's number) $= 6.023 \times 10^{26} \text{ (kmol)}^{-1}$ and with T_c in kelvins, M in kg/kmol, and P_c in N/m², ξ has the units of m²/(N · s) or inverse viscosity. In more convenient units,

$$\xi = 0.176 \left(\frac{T_c}{M^3 P_c^4} \right)^{1/6} \quad (9-4.15)$$

where ξ = reduced, inverse viscosity, $(\mu\text{P})^{-1}$, T_c is kelvins, M is in g/mol, and P_c is in bars.

Equation (9-4.13) has been recommended by several authors (Flynn and Thodos, 1961; Golubev, 1959; Malek and Stiel, 1972; Mathur and Thodos, 1963; Trautz, 1931; and Yoon and Thodos, 1970). The specific form suggested by Lucas (Lucas, 1980; Lucas, 1983; and Lucas, 1984a) is illustrated below.

$$\eta\xi = [0.807 T_r^{0.618} - 0.357 \exp(-0.449T_r) + 0.340 \exp(-4.058 T_r) + 0.018] F_p^o F_Q^o \quad (9-4.16)$$

ξ is defined by Eq. (9-4.15), η is in μP , T_r is the reduced temperature, and F_p^o and F_Q^o are correction factors to account for polarity or quantum effects. To obtain F_p^o , a reduced dipole moment is required. Lucas defines this quantity somewhat differently than did Chung, et al. in Eq. (9-4.12), i.e.,

$$\mu_r = 52.46 \frac{\mu^2 P_c}{T_c^2} \quad (9-4.17)$$

where μ is in debyes, P_c is in bars, and T_c is in kelvins. Then F_p^o values are found as:

$$\begin{aligned} F_p^o &= 1 & 0 \leq \mu_r < 0.022 \\ F_p^o &= 1 + 30.55(0.292 - Z_c)^{1.72} & 0.022 \leq \mu_r < 0.075 \\ F_p^o &= 1 + 30.55(0.292 - Z_c)^{1.72} |0.96 + 0.1(T_r - 0.7)| & 0.075 \leq \mu_r \end{aligned} \quad (9-4.18)$$

The factor F_Q^o is used only for the quantum gases He, H₂, and D₂.

$$F_Q^o = 1.22Q^{0.15} \{1 + 0.00385[(T_r - 12)^2]^{1/M} \text{sign}(T_r - 12)\} \quad (9-4.19)$$

where $Q = 1.38$ (He), $Q = 0.76$ (H₂), $Q = 0.52$ (D₂). Sign() indicates that one should use +1 or -1 depending on whether the value of the argument () is greater than or less than zero.

TABLE 9-2 Comparison between Calculated and Experimental Low-Pressure Gas Viscosities

Compound	T, °C	Experimental value, μP_{\ddagger}	Percent error†		
			Chung et al., Eq. (9-4.10)	Lucas, Eq. (9-4.16)	Reichenberg, Eq. (9-4.21)
Acetic acid	150	118	3.4	—	1.7
	250	151	0.2	—	2.4
Acetylene	30	102	0.6	0.6	2.4
	101	126	-0.6	-0.8	0.7
	200	155	-0.5	-0.6	0.7
Ammonia	37	106	2.2	2.3	—
	147	146	0.4	0.2	—
	267	189	-2.1	-1.9	—
Benzene	28	73.2	1.0	3.2	4.4
	100	92.5	0.2	1.3	2.1
	200	117	0.5	1.6	1.8
	17	145	7.6	8.3	-0.3
Bromotrifluoromethane	97	183	8.2	8.6	-0.5
	37	79	-1.6	1.6	1.6
Isobutane	155	105	2.0	4.7	4.0
	287	132	3.9	6.7	5.6
	7	74	-5.8	-4.1	-5.6
n-butane	127	101	-1.0	0.1	-2.3
	267	132	0.6	1.5	-1.4
	20	76.1	-1.0	1.1	1.8
1-Butene	60	86.3	-0.5	1.4	1.7
	120	102	-0.6	0.9	0.9
	37	154	-0.6	1.6	—
Carbon dioxide	127	194	-0.1	2.2	—
	327	272	0.5	3.0	—
	30	100	0	5.9	—
Carbon disulfide	98.2	125	-1.3	3.5	—
	200	161	-1.9	2.2	—
	125	133	0.8	1.9	-2.8
Carbon tetrachloride	200	156	2.4	3.1	-2.1
	300	186	3.8	4.1	-1.4
	20	133	2.2	3.5	—
Chlorine	100	168	3.3	4.1	—
	200	209	4.5	5.1	—
	20	100	-3.8	3.4	-1.0
Chloroform	100	125	-1.3	5.4	0.6
	300	191	-0.9	5.1	-0.6
	35	72.3	-2.4	-0.1	-4.2
Cyclohexane	100	87.3	-1.4	0.3	-4.1
	300	129	2.6	3.6	-1.9
	20	90.9	-5.2	-1.0	2.0
Dimethyl ether	100	117	-6.1	-2.4	0.2

TABLE 9-2 Comparison between Calculated and Experimental Low-Pressure Gas Viscosities (*Continued*)

Compound	T, °C	Experimental value, $\mu P\ddagger$	Percent error [†]		
			Chung et al., Eq. (9-4.10)	Lucas, Eq. (9-4.16)	Reichenberg, Eq. (9-4.21)
Ethane	47	100	0.1	0.7	-3.2
	117	120	0.2	0.8	-3.3
	247	156	-1.0	-0.3	-4.7
Ethyl acetate	125	101	-2.6	9.0	-1.5
	200	120	-2.4	8.8	-2.0
	300	146	-3.3	7.4	-3.5
Ethanol	110	111	-0.5	-2.5	0.6
	197	137	-0.8	1.6	-0.4
	267	156	-0.3	2.0	-0.1
Diethyl ether	125	99.1	-0.4	0.2	0.7
	200	118	-0.8	-0.5	-0.3
	300	141	-0.6	-0.4	-0.5
<i>n</i> -Hexane	107	81	-1.1	0.9	0.3
	267	116	-2.1	-0.7	-2.1
Methane	-13	98	-0.7	-0.5	—
	147	147	0	-0.9	—
Methyl acetate	125	108	0	10	1.7
	200	157	-1.6	7.6	-1.0
Methanol	67	112	-0.4	-0.9	1.1
	127	132	-0.3	-1.1	1.2
	277	181	-0.3	-1.7	0.9
Methyl chloride	50	119	3.9	0.8	-0.6
	130	147	5.0	1.4	1.9
Nitrogen	27	178	0.3	0.3	—
	227	258	0.3	0.4	—
Isopropanol	157	113	0.3	5.9	3.5
	257	139	0.1	5.4	2.7
Propylene	17	83	2.4	2.4	3.0
	127	115	1.5	0.9	0.8
	307	160	1.7	1.2	0.7
Sulfur dioxide	10	120	2.8	5.5	—
	100	163	0.3	2.2	—
	300	246	-0.2	1.5	—
	700	376	1.5	3.4	—
Toluene	60	78.9	-5.2	-3.7	-2.3
	250	123	-3.5	-3.1	-2.5
Average absolute error			1.9	3.0	1.9

[†] Percent error = [(calc. - exp.)/exp.] \times 100.

[‡] All experimental viscosity values were obtained from Landolt-Bornstein (1955), Lucas (1984), Stephan and Lucas (1979).

Equation (9-4.16) is similar to an equation proposed by Thodos and coworkers (e.g., Yoon and Thodos, 1970). It is interesting to note that, if $T_r \leq 1$, the $f(T_r)$ in brackets in Eq. (9-4.16) is closely approximated by $0.606T_r$, that is,

$$\eta\xi \approx (0.606T_r) F_p^o F_Q^o \quad T_r \leq 1 \quad (9-4.20)$$

The method of Lucas is illustrated in Example 9-2.

Example 9-2 Estimate the viscosity of methanol vapor at a temperature of 550 K and 1 bar by using Lucas' method. The experimental value is 181 μP (Stephan and Lucas, 1979).

solution From Appendix A, $T_c = 512.64$ K, $P_c = 80.97$ bar, $Z_c = 0.224$, $M = 32.042$, and $\mu = 1.7$ debyes. $T_r = 550/512.64 = 1.07$, and $\mu_r = 52.46[(1.7)^2(80.97)/(512.64)^2] = 4.67 \times 10^{-2}$. From Eq. (9-4.18),

$$F_p^o = 1 + (30.55)(0.292 - 0.224)^{1.72} = 1.30$$

With Eq. (9-4.15),

$$\xi = 0.176 \left[\frac{512.64}{(32.042)^2 (80.97)^4} \right]^{1/6} = 4.70 \times 10^{-3} (\mu\text{P})^{-1}$$

Then, with Eq. (9-4.16)

$$\begin{aligned} \eta\xi &= \{(0.807)(1.07)^{0.618} - 0.357 \exp[-(0.449)(1.07)] \\ &\quad + 0.34 \exp[-(4.058)(1.07)] + 0.018\}(1.30) \\ &= 0.836 \end{aligned}$$

$$\eta = \frac{0.836}{(4.70 \times 10^{-3})} = 178 \mu\text{P}$$

$$\text{Error} = \frac{178 - 181}{181} \times 100 = -1.7\%$$

In Table 9-2, experimental viscosities are compared with those computed by Lucas's method. The average absolute error is 3.0%. Even with the correction factor F_p^o , higher errors are noted for polar compounds compared to nonpolar.

Reichenberg (1971, 1979) has suggested an alternate corresponding states relation for low-pressure gas viscosity of organic compounds.

$$\eta = \frac{M^{1/2}T}{a^*[1 + (4/T_c)][1 + 0.36T_r(T_r - 1)]^{1/6}} \frac{T_r(1 + 270 \mu_r^4)}{T_r + 270 \mu_r^4} \quad (9-4.21)$$

η is in μP ; M is the molecular weight; T is the temperature; T_c is the critical temperature, in kelvins; T_r is the reduced temperature; and μ_r , is the reduced dipole moment defined earlier in Eq. (9-4.17). The parameter a^* is defined as

$$a^* = \sum n_i C_i \quad (9-4.22)$$

where n_i represents the number of groups of the i th type and C_i is the group contribution shown in Table 9-3.

The term $(1 + 4/T_c)$ in the denominator of Eq. (9-4.21) may be neglected except for treating quantum gases with low values of T_c .

TABLE 9-3 Values of the Group Contributions C_i for the Estimation of a^* in Eq. (9-4-22) (Reichenberg, 1971)

Group	Contribution C_i
$-\text{CH}_3$	9.04
$\begin{array}{c} \backslash \\ \text{CH}_2 \text{ (nonring)} \\ / \end{array}$	6.47
$\begin{array}{c} \backslash \\ \text{CH} \text{---(nonring)} \\ / \end{array}$	2.67
$\begin{array}{c} \backslash / \\ \text{C} \text{ (nonring)} \\ / \backslash \end{array}$	-1.53
$=\text{CH}_2$	7.68
$=\text{CH} \text{---(nonring)}$	5.53
$\begin{array}{c} \backslash \\ \text{C} \text{= (nonring)} \\ / \end{array}$	1.78
$\equiv\text{CH}$	7.41
$\equiv\text{C} \text{---(nonring)}$	5.24
$\begin{array}{c} \backslash \\ \text{CH}_2 \text{ (ring)} \\ / \end{array}$	6.91
$\begin{array}{c} \backslash \\ \text{CH} \text{---(ring)} \\ / \end{array}$	1.16
$\begin{array}{c} \backslash / \\ \text{C} \text{ (ring)} \\ / \backslash \end{array}$	0.23
$=\text{CH} \text{---(ring)}$	5.90
$\begin{array}{c} \backslash \\ \text{C} \text{= (ring)} \\ / \end{array}$	3.59
$-\text{F}$	4.46
$-\text{Cl}$	10.06
$-\text{Br}$	12.83
$-\text{OH}$ (alcohols)	7.96
$\begin{array}{c} \backslash \\ \text{O} \text{ (nonring)} \\ / \end{array}$	3.59
$\begin{array}{c} \backslash \\ \text{C} \text{=O (nonring)} \\ / \end{array}$	12.02
$-\text{CHO}$ (aldehydes)	14.02
$-\text{COOH}$ (acids)	18.65
$-\text{COO} \text{---(esters) or } \text{HCOO}$ (formates)	13.41
$-\text{NH}_2$	9.71
$\begin{array}{c} \backslash \\ \text{NH (nonring)} \\ / \end{array}$	3.68

TABLE 9-3 Values of the Group Contributions C_i for the Estimation of a^* in Eq. (9-4-22) (Reichenberg, 1971)
(Continued)

Group	Contribution C_i
$=N-(\text{ring})$	4.97
$—CN$	18.15
$\begin{array}{c} \backslash \\ S \text{ (ring)} \\ / \end{array}$	8.86

A comparison between calculated and experimental low-pressure gas viscosity values is given in Table 9-2, and the method is illustrated in Example 9-3.

Example 9-3 Use Reichenberg's method to estimate the viscosity of ethyl acetate vapor at 125°C and low pressure. The experimental value is reported to be 101 μP (Landolt-Bornstein Tabellen, 1955).

solution From Appendix A, $T_c = 523.2$ K, $M = 88.106$, $P_c = 38.3$ bar, and $\mu = 1.9$ debyes. With Eq. (9-4.17),

$$\mu_r = \frac{(52.46)(1.9)^2(38.3)}{(523.2)^2} = 0.0265$$

$$T_r = (125 + 273)/523.2 = 0.761. \text{ With Eq. (9-4.22) and Table 9-3}$$

$$a^* = 2(-\text{CH}_3) + (-\text{CH}_2) + (-\text{COO}-)$$

$$= (2)(9.04) + 6.47 + 13.41 = 37.96$$

With Eq. (9-4.21),

$$\eta = \frac{(88.106)^{1/2}(125 + 273)}{37.96[1 + (0.36)(0.761)(0.761 - 1)]^{1/6}}$$

$$\frac{(0.761)[1 + (270)(0.0265)^4]}{0.761 + (270)(0.0265)^4} = 99.4 \mu\text{P}$$

$$\text{Error} = \frac{99.4 - 101}{101} \times 100 = -1.5\%$$

Recommendations for Estimating Low-pressure Viscosities of Pure Gases

Any of the three estimation methods described in this section may be used with the expectation of errors of 0.5 to 1.5% for nonpolar compounds and 2 to 4% for polar compounds. Lucas's method requires as input data T_c , P_c , and M as well as μ and Z_c for polar compounds and is easy to apply. At present, it is not suitable for highly associated gases like acetic acid, but it could probably be extended by multiplication of an appropriate factor as in the Chung, et al. technique. The Chung, et al. method requires somewhat more input (T_c , V_c , and M and μ , ω , and κ for

the polar correction). The critical volume is less readily available than the critical pressure (See Chap. 2), and the association factor κ is an empirical constant that must be determined from viscosity data. The method is not suited for quantum gases. Reichenberg's technique requires M , T_c , and structural groups as well as μ for the polar correction. This method is not suitable for inorganic gases and cannot be applied to organic gases for which necessary group contributions have not been determined.

9-5 VISCOSITIES OF GAS MIXTURES AT LOW PRESSURES

The rigorous kinetic theory of Chapman and Enskog can be extended to determine the viscosity of low-pressure multicomponent mixtures (Brokaw, 1964, 1965, 1968, 1965; Chapman and Cowling, 1939; Hirschfelder, et al., 1954; Kestin, et al., 1976). The final expressions are quite complicated and are rarely used to estimate mixture viscosities. Three simplifications of the rigorous theoretical expressions are described below. Reichenberg's equations are the most complex, but, as shown later, the most consistently accurate. Wilke's method is simpler, and that of Herning and Zipperer is even more so. All these methods are essentially interpolative; i.e., the viscosity values for the pure components must be available. The methods then lead to estimations showing how the mixture viscosity varies with composition. Later in this section, two corresponding states methods are described; they do not require pure component values as inputs. A compilation of references dealing with gas mixture viscosities (low and high pressure) has been prepared by Sutton (1976).

Method of Reichenberg (1974, 1977, 1979)

In this technique, Reichenberg has incorporated elements of the kinetic theory approach of Hirschfelder, et al. (1954) with corresponding states methodology to obtain desired parameters. In addition, a polar correction has been included. The general, multicomponent mixture viscosity equation is:

$$\eta_m = \sum_{i=1}^n K_i \left(1 + 2 \sum_{j=1}^{i-1} H_{ij} K_j + \sum_{j=1 \neq i}^n \sum_{k=1 \neq i}^n H_{ij} H_{ik} K_j K_k \right) \quad (9-5.1)$$

where η_m is the mixture viscosity and n is the number of components. With η_i the viscosity of pure i , M_i the molecular weight of i , and y_i the mole fraction of i in the mixture,

$$K_i = \frac{y_i \eta_i}{y_i + \eta_i \sum_{k=1 \neq i}^n y_k H_{ik} [3 + (2M_k/M_i)]} \quad (9-5.2)$$

Two other component properties used are:

$$U_i = \frac{[1 + 0.36T_{ri}(T_{ri} - 1)]^{1/6} F_{Ri}}{(T_{ri})^{1/2}} \quad (9-5.3)$$

$$C_i = \frac{M_i^{1/4}}{(\eta_i U_i)^{1/2}} \quad (9-5.4)$$

where $T_{ri} = T/T_{ci}$ and F_{Ri} is a polar correction.

$$F_{Ri} = \frac{T_{ri}^{3.5} + (10 \mu_{ri})^7}{T_{ri}^{3.5}[1 + (10 \mu_{ri})^7]} \quad (9-5.5)$$

Here μ_{ri} is the reduced dipole moment of i and is calculated as shown earlier in Eq. (9-4.17). For the term $H_{ij} = H_{ji}$,

$$H_{ij} = \left[\frac{M_i M_j}{32(M_i + M_j)^3} \right]^{1/2} (C_i + C_j)^2 \times \frac{[1 + 0.36T_{rij}(T_{rij} - 1)]^{1/6} F_{Rij}}{(T_{rij})^{1/2}} \quad (9-5.6)$$

with

$$T_{rij} = \frac{T}{(T_{ci} T_{cj})^{1/2}} \quad (9-5.7)$$

F_{Rij} is found from Eq. (9-5.5) with T_{ri} replaced by T_{rij} and μ_{ri} by $\mu_{rij} = (\mu_{ri} \mu_{rj})^{1/2}$. For a binary gas mixture of 1 and 2, these equations may be written as:

$$\eta_m = K_1(1 + H_{12}^2 K_2^2) + K_2(1 + 2 H_{12} K_1 + H_{12}^2 K_1^2) \quad (9-5.8)$$

$$K_1 = \frac{y_1 \eta_1}{y_1 + \eta_1 \{y_2 H_{12} [3 + (2 M_2/M_1)]\}} \quad (9-5.9)$$

$$K_2 = \frac{y_2 \eta_2}{y_2 + \eta_2 \{y_1 H_{12} [3 + (2 M_1/M_2)]\}} \quad (9-5.10)$$

$$U_1 = \frac{[1 + 0.36T_{r1}(T_{r1} - 1)]^{1/6}}{T_{r1}^{1/2}} \frac{T_{r1}^{3.5} + (10 \mu_{r1})^7}{T_{r1}^{3.5}[1 + (10 \mu_{r1})^7]} \quad (9-5.11)$$

and a comparable expression for U_2 . The meaning of C_1 and C_2 is clear from Eq. (9-5.4). Finally, with

$$\begin{aligned} T_{r12} &= \frac{T}{(T_{c1} T_{c2})^{1/2}} \quad \text{and} \quad \mu_{r12} = (\mu_{r1} \mu_{r2})^{1/2} \\ H_{12} &= \frac{(M_1 M_2 / 32)^{1/2} [1 + 0.36T_{r12}(T_{r12} - 1)]^{1/6}}{(M_1 + M_2)^{3/2} (T_{r12})^{1/2}} \\ &\quad \times (C_1 + C_2)^2 \frac{T_{r12}^{3.5} + (10 \mu_{r12})^7}{T_{r12}^{3.5}[1 + (10 \mu_{r12})^7]} \end{aligned} \quad (9-5.12)$$

To employ Reichenberg's method, for each component one needs the pure gas viscosity at the system temperature as well as the molecular weight, dipole moment, critical temperature, and critical pressure. The temperature and composition are state variables.

The method is illustrated in Example 9-4. A comparison of experimental and calculated gas-mixture viscosities is shown in Table 9-4.

TABLE 9-4 Comparison of Calculated and Experimental Low-Pressure Gas Mixture Viscosities

System	T, K	Mole fraction first component	Viscosity (exp.) μP	Ref.*	Percent deviation† calculated by method of:				
					Reichenberg, Eq. (9-5.8)	Wilke, Eq. (9-5.16)	Herning and Zipperer, Eq. (9-5.17)	Lucas, Eq. (9-4.16) with Eqs. (9-5.18) through (9-5.23)	Chung, et al., Eq. (9-5.24)
Nitrogen-hydrogen	373	0.0	104.2	6, 11	—	—	—	0.8	-11
		0.2	152.3		4.3	12	2.0	2.1	-23
		0.51	190.3		1.8	5.6	-1.0	-2.0	-11
		0.80	205.8		0.1	1.4	-1.2	3.6	-3.3
		1.0	210.1		—	—	—	0.4	0
Methane-propane	298	0.0	81.0	1	—	—	—	3.5	1.3
		0.2	85.0		0.2	-0.3	-0.2	4.6	1.7
		0.4	89.9		0.1	-0.8	-0.6	5.0	1.7
		0.6	95.0		0.6	-0.4	-0.2	5.4	1.9
		0.8	102.0		0.2	-0.6	-0.5	3.7	1.0
		1.0	110.0		—	—	—	0.3	1.0
		0.0	131.0		—	—	—	4.0	2.3
		0.2	136.0		0.4	0.0	-0.2	5.2	2.7
Carbon tetrafluoride-sulfur hexafluoride	303	0.4	142.0	8	0.6	0.0	-0.5	5.6	2.6
		0.6	149.0		0.7	0.0	-0.6	5.2	2.0
		0.8	157.0		0.7	0.0	-0.3	3.7	1.1
		1.0	167.0		—	—	—	-0.2	0.2
		0.0	159.0		—	—	—	6.6	0.7
		0.257	159.9		2.0	2.0	1.8	9.3	3.8
		0.491	161.5		3.4	3.4	3.1	11.0	6.2
		0.754	164.3		4.6	4.6	4.3	13.0	8.4
		1.0	176.7		—	—	—	7.4	3.6

TABLE 9-4 Comparison of Calculated and Experimental Low-Pressure Gas Mixture Viscosities (*Continued*)

					Percent deviation† calculated by method of:				
System	T, K	Mole fraction first component	Viscosity (exp.) μP	Ref.*	Reichenberg, Eq. (9-5.8)	Wilke, Eq. (9-5.16)	Herning and Zipperer, Eq. (9-5.17)	Lucas, Eq. (9-4.16) with Eqs. (9-5.18) through (9-5.23)	Chung, et al., Eq. (9-5.24)
Nitrogen-carbon dioxide	293	0.0	146.6	5	—	—	—	1.6	-1.2
		0.213	153.5		0.5	-1.3	-1.0	0.4	-0.3
		0.495	161.8		0.4	-1.8	-1.5	-0.2	0.7
		0.767	172.1		-2.0	-2.8	-2.5	-1.7	-0.7
Ammonia-hydrogen	306	1.0	175.8	6	—	—	—	0.4	-0.2
		0.0	90.6		—	—	—	2.4	-9.9
		0.195	118.4		-4.0	-11	-18	-2.7	2.1
		0.399	123.8		-4.6	-12	-19	-3.0	10.0
Hydrogen sulfide-ethyl ether	331	0.536	122.4	7	-4.5	-11	-16	-2.7	10.0
		0.677	120.0		-4.8	-9.7	-14	-3.1	7.1
		1.0	105.9		—	—	—	1.3	0.9
		0.0	84.5		—	—	—	-1.7	-4.0
Ammonia-methylamine	423	0.204	87	2	-2.9	-3.2	0.2	2.3	0.4
		0.500	97		-2.2	-2.8	3.2	3.4	1.7
		0.802	116		0.0	-0.4	4.2	0.6	-0.7
		1.0	137		—	—	—	-3.0	-4.1
Ammonia-methylamine	673	0.0	130.0	2	—	—	—	-2.1	-8.0
		0.25	134.5		-0.8	-0.3	-0.6	-1.5	-7.5
		0.75	142.2		-1.0	-0.3	-0.7	0.1	-3.4
		1.0	146.0		—	—	—	1.1	1.1
	673	0.0	204.8	2	—	—	—	-4.6	-11
		0.25	212.8		-2.6	-0.7	-0.9	-4.9	-11
		0.75	228.3		-3.1	-0.7	-0.9	-4.7	-9.3
		1.0	235.0		—	—	—	-4.3	-5.4

Nitrogen-monochlorodi-fluoromethane	323	0.0	134	10	—	—	—	—	11.0	6.0
		0.286	145		0.8	—	—	—	11.0	7.3
		0.463	153		1.3	—	—	—	11.0	7.4
		0.644	164		0.7	—	—	—	8.9	5.6
		0.824	177		—	—	—	—	5.0	2.4
Nitrous oxide-sulfur dioxide	353	1.0	188		—	—	—	—	0.8	0.4
		0.0	152.3	4	—	—	—	—	3.9	—1.5
		0.325	161.7		—1.7	—	—	—	0.6	—1.6
		0.625	167.8		—1.6	—	—	—	—0.6	—2.3
		0.817	170.7		—0.9	—	—	—	—0.7	—1.9
Nitrogen- <i>n</i> -heptane	344	1.0	173.0		—	—	—	—	—0.6	—0.7
		0.0	69.4	3, 9	—	—	—	—	0.8	—3.5
		0.515	104.0		0.7	—	—	—	—0.2	—4.8
		0.853	154.6		0.9	—	—	—	—0.5	—3.2
		1.0	197.5		—	—	—	—	0.6	0.2

[†]Percent deviation = [(calc. — exp.)/(exp.)] × 100.

*References: 1, Bircher, 1943; 2, Burch and Raw, 1967; 3, Carmichael and Sage, 1966; 4, Chakraborti and Gray, 1965; 5, Kestin and Leidenfrost, 1959; 6, Pal and Baruna, 1967; 7, Pal and Bhattacharyya, 1969; 8, Raw and Tang, 1963; 9, Stephan and Lucas, 1979; 10, Tanka, et al., 1977; 11, Trautz and Baumann, 1929.

Example 9-4 Use Reichenberg's method to estimate the viscosity of a nitrogen-monochlorodifluoromethane (R-22) mixture at 50°C and atmospheric pressure. The mole fraction nitrogen is 0.286. The experimental viscosity is 145 μP (Tanaka, et al., 1977).

solution The following pure component properties are used:

	N_2	CHClF_2
T_c , K	126.2	369.28
P_c , bar	33.98	49.86
M , g/mol	28.014	86.468
μ , debyes	0	1.4
η , 50°C, μP	188	134

With $T = 50^\circ\text{C}$, $T_r(\text{N}_2) = 2.56$, and $T_r(\text{CHClF}_2) = 0.875$,

$$T_{r12} = \frac{50 + 273.2}{[(126.2)(369.3)]^{1/2}} = 1.497$$

$\mu_r(\text{N}_2) = 0$, and from Eq. (9-4.17),

$$\mu_r(\text{CHClF}_2) = \frac{(52.46)(1.4)^2(49.86)}{(369.28)^2} = 0.0376$$

Since $\mu_{r12} = (\mu_{r1}\mu_{r2})^{1/2}$, then for this mixture, $\mu_{r12} = 0$. With Eq. (9-5.11), for CHClF_2 ,

$$U(\text{CHClF}_2) = \frac{[1 + (0.36)(0.875)(0.875 - 1)]^{1/6}}{(0.875)^{1/2}} \times \frac{(0.875)^{3.5} + (10)^7(0.0376)^7}{(0.875)^{3.5}[1 + (10)^7(0.0376)^7]}$$

$$= 1.063$$

and $U(\text{N}_2) = 0.725$

$$\text{Then, } C(\text{N}_2) = \frac{(28.014)^{1/4}}{[(188)(0.725)]^{1/2}} = 0.197$$

and $C(\text{CHClF}_2) = 0.256$

Next,

$$H(\text{N}_2\text{---CHClF}_2) = (0.197 + 0.256)^2 \frac{[(28.014)(86.468)]^{1/2}}{[32(28.014 + 86.468)^3]^{1/2}}$$

$$\times \frac{[1 + (0.36)(1.497)(1.497 - 1)]^{1/6}}{(1.497)^{1/2}} \times 1.0$$

$$= 1.237 \times 10^{-3}$$

$$K(\text{N}_2) = \frac{(0.286)(188)}{0.286 + (188)(0.714)(1.237 \times 10^{-3})\{3 + [(2)(86.469)/28.014]\}} = 29.71$$

and $K(\text{CHClF}_2) = 107.9$. Substituting into Eq. (9-5.8),

$$\begin{aligned}\eta_m &= (29.71)[1 + (1.237 \times 10^{-3})^2(107.9)^2] + (107.9)[1 \\ &\quad + (2)(1.237 \times 10^{-3})(29.71) + (1.237 \times 10^{-3})^2(29.71)^2] \\ &= 146.2 \mu\text{P} \\ \text{Error} &= \frac{146.2 - 145}{145} \times 100 = 0.8\%\end{aligned}$$

Method of Wilke (1950)

In a further simplification of the kinetic theory approach, Wilke (1950) neglected second-order effects and proposed:

$$\eta_m = \frac{\sum_{i=1}^n \frac{y_i \eta_i}{\sum_{j=1}^n y_j \phi_{ij}} \quad (9-5.13)$$

where

$$\phi_{ij} = \frac{[1 + (\eta_i/\eta_j)^{1/2}(M_j/M_i)^{1/4}]^2}{[8(1 + M_i/M_j)]^{1/2}} \quad (9-5.14)$$

ϕ_{ji} is found by interchanging subscripts or by

$$\phi_{ji} = \frac{\eta_j}{\eta_i} \frac{M_i}{M_j} \phi_{ij} \quad (9-5.15)$$

For a binary system of 1 and 2, with Eqs. (9-5.13) to (9-5.15),

$$\eta_m = \frac{y_1 \eta_1}{y_1 + y_2 \phi_{12}} + \frac{y_2 \eta_2}{y_2 + y_1 \phi_{21}} \quad (9-5.16)$$

where η_m = viscosity of the mixture

η_1, η_2 , = pure component viscosities

y_1, y_2 = mole fractions

and

$$\begin{aligned}\phi_{12} &= \frac{[1 + (\eta_1/\eta_2)^{1/2}(M_2/M_1)^{1/4}]^2}{\{8[1 + (M_1/M_2)]\}^{1/2}} \\ \phi_{21} &= \phi_{12} \frac{\eta_2 M_1}{\eta_1 M_2}\end{aligned}$$

Equation (9-5.13), with ϕ_{ij} from Eq. (9-5.14), has been extensively tested. Wilke (1950) compared values with data on 17 binary systems and reported an average deviation of less than 1%; several cases in which η_m passed through a maximum were included. Many other investigators have tested this method (Amdur and Mason, 1958; Bromley and Wilke, 1951; Cheung, 1958; Dahler, 1959; Gandhi and Saxena, 1964; Ranz and Brodowsky, 1962; Saxena and Gambhir, 1963, 1963a;

Strunk, et al., 1964; Vanderslice, et al. 1962; Wright and Gray, 1962). In most cases, only nonpolar mixtures were compared, and very good results obtained. For some systems containing hydrogen as one component, less satisfactory agreement was noted. In Table 9-4, Wilke's method predicted mixture viscosities that were larger than experimental for the H_2-N_2 system, but for H_2-NH_3 , it underestimated the viscosities. Gururaja, et al. (1967) found that this method also overpredicted in the H_2-O_2 case but was quite accurate for the H_2-CO_2 system. Wilke's approximation has proved reliable even for polar-polar gas mixtures of aliphatic alcohols (Reid and Belenyessy, 1960). The principal reservation appears to lie in those cases where $M_i \gg M_j$ and $\eta_i \gg \eta_j$.

Example 9-5 Kestin and Yata (1968) report that the viscosity of a mixture of methane and *n*-butane is 93.35 μP at 293 K when the mole fraction of *n*-butane is 0.303. Compare this result with the value estimated by Wilke's method. For pure methane and *n*-butane, these same authors report viscosities of 109.4 and 72.74 μP .

solution Let 1 refer to methane and 2 to *n*-butane. $M_1 = 16.043$ and $M_2 = 58.123$.

$$\phi_{12} = \frac{[1 + (109.4/72.74)^{1/2}(58.123/16.043)^{1/4}]^2}{\{8[1 + (16.043/58.123)]\}^{1/2}} = 2.268$$

$$\phi_{21} = 2.268 \frac{72.74}{109.4} \frac{16.043}{58.123} = 0.416$$

$$\begin{aligned} \eta_m &= \frac{(0.697)(109.4)}{0.697 + (0.303)(2.268)} + \frac{(0.303)(72.74)}{0.303 + (0.697)(0.416)} \\ &= 92.26 \mu P \end{aligned}$$

$$\text{Error} = \frac{92.26 - 93.35}{93.35} \times 100 = -1.2\%$$

Herning and Zipperer (1936) Approximation of ϕ_{ij}

As an approximate expression for ϕ_{ij} of Eq. (9-5.14) the following is proposed (Herning and Zipperer, 1936):

$$\phi_{ij} = \left(\frac{M_j}{M_i} \right)^{1/2} = \phi_{ji}^{-1} \quad (9-5.17)$$

When Eq. (9-5.17) is used with Eq. (9-5.16) to estimate low-pressure binary gas mixture viscosities, quite reasonable predictions are obtained (Table 9-4) except for systems such as H_2-NH_3 . The technique is illustrated in Example 9-6. Note that Examples 9-5 and 9-6 treat the same problem; each provides a viscosity estimate close to the experimental value. But the ϕ_{12} and ϕ_{21} values employed in the two cases are quite different. Apparently, multiple sets of ϕ_{ij} and ϕ_{ji} work satisfactorily in Eq. (9-5.13).

Example 9-6 Repeat Example 9-5 by using the Herning and Zipperer approximation for ϕ_{ij} .

solution As before, with 1 as methane and 2 as *n*-butane

$$\phi_{12} = \left(\frac{58.123}{16.043} \right)^{1/2} = 1.903$$

$$\phi_{21} = \phi_{12}^{-1} = 0.525$$

$$\eta_m = \frac{(0.697)(109.4)}{0.697 + (0.303)(1.903)} + \frac{(0.303)(72.74)}{0.303 + (0.697)(0.525)} = 92.82 \mu \text{ P}$$

$$\text{Error} = \frac{92.82 - 93.35}{93.35} \times 100 = -0.6\%$$

Corresponding States Methods

In this approach, one estimates pseudocritical and other mixture properties (See Sec. 5-3) from pure component properties, the composition of the mixture, and appropriate combining and mixing rules.

Lucas (1980, 1983, 1984a) Rules

Lucas (1980, 1983, 1984a) defined mixture properties as shown below for use in Eqs. (9-4.15) through (9-4.19).

$$T_{cm} = \sum_i y_i T_{ci} \quad (9-5.18)$$

$$P_{cm} = RT_{cm} \frac{\sum_i y_i Z_{ci}}{\sum_i y_i V_{ci}} \quad (9-5.19)$$

$$M_m = \sum_i y_i M_i \quad (9-5.20)$$

$$F_{pm}^o = \sum_i y_i F_{pi}^o \quad (9-5.21)$$

$$F_{Qm}^o = \left(\sum_i y_i F_{Qi}^o \right) A \quad (9-5.22)$$

and, letting the subscript *H* denote the mixture component of highest molecular weight and *L* the component of lowest molecular weight,

$$A = 1 - 0.01 \left(\frac{M_H}{M_L} \right)^{0.87} \quad \text{for } \frac{M_H}{M_L} > 9 \text{ and } 0.05 < y_H < 0.7; \quad (9-5.23)$$

otherwise, $A = 1$

The method of Lucas does not necessarily lead to the pure component viscosity η_i when all $y_j = 0$ except $y_i = 1$. Thus the method is not interpolative in the same way as are the techniques of Reichenberg, Wilke, and Herning and Zipperer. Nev-

ertheless, as seen in Table 9-4, the method provides reasonable estimates of η_m in most test cases.

Example 9-7 Estimate the viscosity of a binary mixture of ammonia and hydrogen at 33°C and low pressure by using the Lucas corresponding states method.

solution Let us illustrate the method for a mixture containing 67.7 mole percent ammonia. We use the following pure-component values:

	Ammonia	Hydrogen
T_c , K	405.50	33.2
P_c , bar	113.5	13.0
V_c , cm ³ /mol	72.5	64.3
Z_c	0.244	0.306
M	17.031	2.016
μ , debyes	1.47	0
T_r	0.755	9.223

Using Eqs. (9-5.18) to (9-5.20), $T_{cm} = 285.2$ K, $P_{cm} = 89.6$ bar, and $M_m = 12.18$. From these values and Eq. (9-4.15), $\xi_m = 6.46 \times 10^{-3} (\mu\text{P})^{-1}$. With Eq. (9-4.17), $\mu_r(\text{NH}_3) = 7.825 \times 10^{-2}$ and $\mu_r(\text{H}_2) = 0$. Then, with Eq. (9-4.18),

$$F_p^o(\text{NH}_3) = 1 + 30.55(0.292 - 0.244)^{1.72} |0.96 + 0.1(0.755 - 0.7)| = 1.159$$

$$F_p^o(\text{H}_2) = 1.0$$

$$F_{pm}^o = (1.159)(0.677) + (1)(0.323) = 1.107$$

For the quantum correction, with Eq. (9-5.23), since $M_H/M_L = 17.031/2.016 = 8.4 < 9$, then $A = 1$. $F_Q^o(\text{NH}_3) = 1.0$, and with Eq. (9-4.19),

$$\begin{aligned} F_Q^o(\text{H}_2) &= (1.22)(0.76)^{0.15} \{1 + 0.00385[(9.209 - 12)^2]^{1/2.016} \\ &\quad \times \text{sign}(9.209 - 12)\} \\ &= (1.171)[1 + (0.01061)(-1)] = 1.158 \end{aligned}$$

$$F_{Qm}^o = (1.158)(0.323) + (1)(0.677) = 1.051$$

Next, from Eq. (9-4.16) with $T_{rm} = (33 + 273.2)/285.3 = 1.073$

$$\eta_m \xi_m = (0.645)(1.107)(1.051) = 0.750$$

$$\eta_m = \frac{0.750}{6.46 \times 10^{-3}} = 116.1 \mu\text{P}$$

The experimental value is 120.0 μP ; thus

$$\text{Error} = \frac{116.1 - 120.0}{120.0} \times 100 = -3.2\%$$

The viscosity of the ammonia-hydrogen mixture at 33°C is line 3 in Fig. 9-3.

Chung, et al. rules (1984, 1988)

In this case, Eq. (9-3.9) is employed to estimate the mixture viscosity with, however, a factor F_{cm} as used in Eq. (9-4.10) to correct for shape and polarity.

$$\eta_m = \frac{26.69 F_{cm}(M_m T)^{1/2}}{\sigma_m^2 \Omega_v} \quad (9-5.24)$$

where $\Omega_v = f(T_m^*)$. In the Chung, et al. approach, the mixing rules are:

$$\sigma_m^3 = \sum_i \sum_j y_i y_j \sigma_{ij}^3 \quad (9-5.25)$$

$$T_m^* = \frac{T}{(\varepsilon/k)_m} \quad (9-5.26)$$

$$\left(\frac{\varepsilon}{k}\right)_m = \frac{\sum_i \sum_j y_i y_j (\varepsilon_{ij}/k) \sigma_{ij}^3}{\sigma_m^3} \quad (9-5.27)$$

$$M_m = \left[\frac{\sum_i \sum_j y_i y_j (\varepsilon_{ij}/k) \sigma_{ij}^2 M_{ij}^{1/2}}{(\varepsilon/k)_m \sigma_m^2} \right]^2 \quad (9-5.28)$$

$$\omega_m = \frac{\sum_i \sum_j y_i y_j \omega_{ij} \sigma_{ij}^3}{\sigma_m^3} \quad (9-5.29)$$

$$\mu_m^4 = \sigma_m^3 \sum_i \sum_j \left(\frac{y_i y_j \mu_i^2 \mu_j^2}{\sigma_{ij}^3} \right) \quad (9-5.30)$$

$$\kappa_m = \sum_i \sum_j y_i y_j \kappa_{ij} \quad (9-5.31)$$

and the combining rules are:

$$\sigma_{ii} = \sigma_i = 0.809 V_{ci}^{1/3} \quad (9-5.32)$$

$$\sigma_{ij} = \xi_{ij} (\sigma_i \sigma_j)^{1/2} \quad (9-5.33)$$

$$\frac{\varepsilon_{ii}}{k} = \frac{\varepsilon_i}{k} = \frac{T_{ci}}{1.2593} \quad (9-5.34)$$

$$\frac{\varepsilon_{ij}}{k} = \zeta_{ij} \left(\frac{\varepsilon_i}{k} \frac{\varepsilon_j}{k} \right)^{1/2} \quad (9-5.35)$$

$$\omega_{ii} = \omega_i \quad (9-5.36)$$

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \quad (9-5.36)$$

$$\kappa_{ii} = \kappa_i \quad (9-5.37)$$

$$\kappa_{ij} = (\kappa_i \kappa_j)^{1/2} \quad (9-5.38)$$

$$M_{ij} = \frac{2M_i M_j}{M_i + M_j} \quad (9-5.39)$$

$$(9-5.40)$$

ξ_{ij} and ζ_{ij} are binary interaction parameters which are normally set equal to unity. The F_{cm} term in Eq. (9-5.24) is defined as in Eq. (9-4.11).

$$F_{cm} = 1 - 0.275\omega_m + 0.059035 \mu_{rm}^4 + \kappa_m \quad (9-5.41)$$

where μ_{rm} is as in Eq. (9-4.12)

$$\mu_{rm} = \frac{131.3 \mu_m}{(V_{cm} T_{cm})^{1/2}} \quad (9-5.42)$$

$$V_{cm} = (\sigma_m/0.809)^3 \quad (9-5.43)$$

$$T_{cm} = 1.2593 \left(\frac{\varepsilon}{k} \right)_m \quad (9-5.44)$$

In these equations, T_c is in kelvins, V_c is in cm^3/mol and μ is in debyes.

The rules suggested by Chung, et al. are illustrated for a binary gas mixture in Example 9-8. As with the Lucas approach, the technique is not interpolative between pure component viscosities. Some calculated binary gas mixture viscosities are compared with experimental values in Table 9-4. Errors vary, but they are usually less than about $\pm 5\%$.

Example 9-8 Use the Chung, et al. method to estimate the low-pressure gas viscosity of a binary of hydrogen sulfide and ethyl ether containing 20.4 mole percent H_2S . The temperature is 331 K.

solution The properties listed below are from Appendix A, the problem statement, and Table 9-1:

	Hydrogen sulfide	Ethyl ether
T_c , K	373.4	466.70
V_c , cm^3/mol	98	280
ω	0.090	0.281
μ , debyes	0.9	1.3
κ	0	0
M , g/mol	34.082	74.123
y	0.204	0.796

From Eqs. (9-5.32) and (9-5.33),

$$\sigma(\text{H}_2\text{S}) = (0.809)(98)^{1/3} = 3.730 \text{ \AA}$$

$$\sigma(\text{EE}) = 5.293 \text{ \AA}$$

$$\sigma(\text{H}_2\text{S-EE}) = 4.443 \text{ \AA}$$

Then, with Eq. (9-5.25),

$$\sigma_m^3 = (0.204)^2(3.730)^3 + (0.796)^2(5.293)^3 + (2)(0.204)(0.796)(4.443)^3 = 124.58 \text{ \AA}^3$$

From Eqs. (9-5.34) and (9-5.35)

$$\frac{\varepsilon}{k} = (\text{H}_2\text{S}) = \frac{373.4}{1.2593} = 296.5 \text{ K}$$

$$\frac{\varepsilon}{k} (\text{EE}) = 370.6 \text{ K}$$

$$\frac{\varepsilon}{k} (\text{H}_2\text{S-EE}) = 331.5 \text{ K}$$

Then, with Eq. (9-5.27),

$$\left(\frac{\varepsilon}{k}\right)_m = [(0.204)^2(296.5)(3.730)^3 + (0.796)^2(370.6)(5.293)^3 + (2)(0.204)(0.796)(331.5)(4.443)^3] / 124.58 = 360.4 \text{ K}$$

With Eqs. (9-5.28) and (9-5.40),

$$M_m = \{ (0.204)^2(296.5)(3.730)^2(34.082)^{1/2} + (0.796)^2(370.6)(5.293)^2(74.123)^{1/2} + (2)(0.204)(0.796)(331.5)(4.443)^2[(2)(34.082)(74.123)/(34.082 + 74.123)]^{1/2} \} / (360.4)(124.58)^{2/3} = 64.44 \text{ g/mol}$$

With Eq. (9-5.29),

$$\omega_m = \{ (0.204)^2(0.090)(3.730)^3 + (0.796)^2(0.281)(5.293)^3 + (2)(0.204)(0.796)[(0.090 + 0.281)/2](4.443)^3 \} / 124.58 = 0.256$$

and with Eq. (9-5.30),

$$\mu_m^4 = \{ [(0.204)^2(0.9)^4/(3.730)^3] + [(0.796)^2(1.3)^4/(5.293)^3] + [(2)(0.204)(0.796)(0.9)^2(1.3)^2/(4.443)^3] \} (124.58) = 2.218$$

$$\mu_m = 1.22 \text{ debyes}$$

so, with Eqs. (9-5.42) to (9-5.44),

$$V_{cm} = \frac{(124.58)}{(0.809)^3} = 235.3 \text{ cm}^3/\text{mol}$$

$$T_{cm} = (1.2593)(360.4) = 453.9 \text{ K}$$

$$\mu_{rm} = \frac{(131.3)(1.22)}{[(235.3)(453.9)]^{1/2}} = 0.490$$

Since $\kappa_m = 0$, with Eq. (9-5.41),

$$F_{cm} = 1 - (0.275)(0.256) + (0.059035)(0.490)^4 = 0.933$$

Using T_m^* from Eq. (9-5.26) [= 331/360.4 = 0.918] and Eq. (9-4.3), $\Omega_v = 1.664$. Finally, with Eq. (9-5.24),

$$\eta_m = \frac{(26.69)(0.933)[(64.44)(331)]^{1/2}}{(124.58)^{2/3}(1.664)} = 87.6 \mu\text{P}$$

The experimental value is 87 μP (Table 9-4).

$$\text{Error} = \frac{87.6 - 87}{87} \times 100 = 0.4\%$$

Discussion and Recommendations to Estimate the Low-pressure Viscosity of Gas Mixtures

As is obvious from the estimation methods discussed in this section, the viscosity of a gas mixture can be a complex function of composition. This is evident from Fig. 9-3. There may be a maximum in mixture viscosity in some cases, e.g., system 3, ammonia-hydrogen. However, cases of a viscosity minimum have been reported.

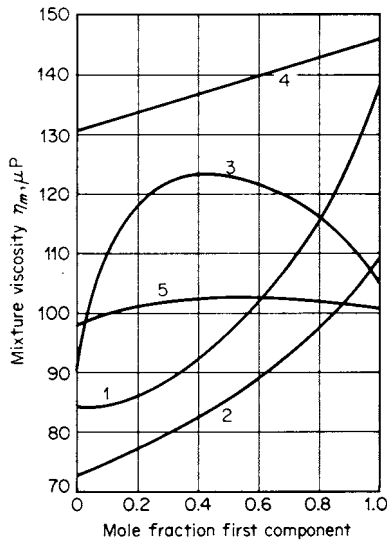


FIGURE 9-3 Gas mixture viscosities.

No.	System	Reference
1	Hydrogen sulfide-ethyl ether	Pal and Bhattacharyya (1969)
2	Methane- <i>n</i> -butane	Kestin and Yata (1968)
3	Ammonia-hydrogen	Pal and Barua (1967)
4	Ammonia-methyl amine	Burch and Raw (1967)
5	Ethylene-ammonia	Trautz and Heberling (1931)

Behavior similar to that of the ammonia-hydrogen case occurs most often in polar-nonpolar mixtures in which the pure component viscosities are not greatly different (Hirschfelder, et al., 1960; Rutherford, et al., 1960). Maxima are more pronounced as the molecular weight ratio differs from unity.

Of the five estimation methods described in this section, three (Herning and Zipperer, Wilke, and Reichenberg) use the kinetic theory approach and yield interpolative equations between the pure component viscosities. Reichenberg's method is most consistently accurate, but it is the most complex. To use Reichenberg's procedure, one needs, in addition to temperature and composition, the viscosity, critical temperature, critical pressure, molecular weight, and dipole moment of each constituent. Wilke's and Herning and Zipperer's methods require only the pure component viscosities and molecular weights; these latter two yield reasonably accurate predictions of the mixture viscosity.

Arguing that it is rare to have available the pure gas viscosities at the temperature of interest, both Lucas and Chung, et al. provide estimation methods to cover the entire range of composition. At the end points where only pure components exist, their methods reduce to those described earlier in Sec. 9-3. Although the errors from these two methods are, on the average, slightly higher than those of the interpolative techniques, they are usually less than $\pm 5\%$ as seen from Table 9-4. Such errors could be reduced even further if pure component viscosity data were available and were employed in a simple linear correction scheme. For example, if the pure component viscosity predictions are too high, the mixture prediction would be improved if it were lowered by composition-averaged error of the pure component predictions.

An estimation method recently proposed by Davidson (1993) was judged as effective as those discussed in this section.

It is recommended that Reichenberg's method [Eq. (9-5.8)] be used to calculate η_m if pure component viscosity values are available. Otherwise, either the Lucas method [Eq. (9-4.16)] or the Chung, et al. method [Eq. (9-5.24)] can be employed if critical properties are available for all components.

9-6 EFFECT OF PRESSURE ON THE VISCOSITY OF PURE GASES

Figure 9-4 shows the viscosity of carbon dioxide ($T_c = 304.1$ K and $P_c = 73.8$ bar) as a function of temperature and pressure. In some ranges ($T_r > 1.5$ and $P_r < 2$), pressure has little effect on viscosity. But when $1 < T_r < 1.5$ and when $P > P_c$, pressure has a strong effect on viscosity as can be seen by the nearly vertical isobars in this region of Fig. 9-4. Figure 9-4 shows isobars as a function of temperature, while Fig. 9-5 shows isotherms as a function of pressure for nitrogen ($T_c = 77.4$ K, $P_c = 33.9$ bar). Lucas (1981, 1983) has generalized the viscosity phase diagrams (for nonpolar gases) as shown in Fig. 9-6. In this case, the ordinate is $\eta\xi$ and the temperatures and pressures are reduced values. ξ is the inverse reduced viscosity defined earlier in Eq. (9-4.15).

At the critical point, the viscosity diverges so that its value is larger than would otherwise be expected. However, this effect is much smaller for viscosity than for thermal conductivity (see Fig. 10-5). Whereas the thermal conductivity can increase by a factor of two near the critical point, the increase in viscosity is on the order

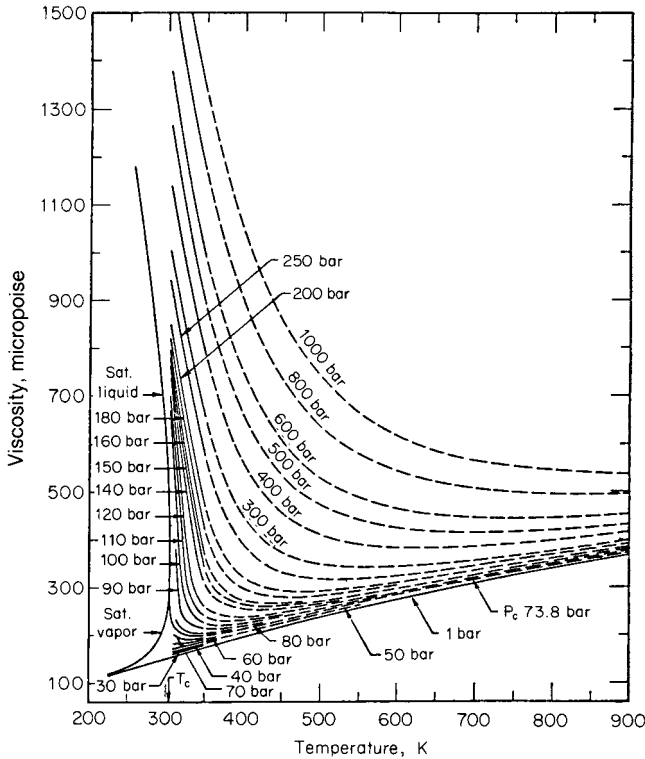


FIGURE 9-4 Viscosity of carbon dioxide. (Stephan and Lucas, 1979)

of 1%. In fact Vesovic, et al. (1990) state that for carbon dioxide, “the viscosity enhancement is less than 1% at densities and temperatures outside the range bounded approximately by $300\text{K} < T < 310\text{K}$ and $300\text{ kg m}^{-3} < \rho < 600\text{ kg m}^{-3}$.”

In Fig. 9-6, the lower limit of the P_r curves would be indicative of the dilute-gas state, as described in Sec. 9-4. In such a state, η increases with temperature. At high reduced pressures, we see there is a wide range of temperatures where η decreases with temperature. In this region the viscosity behavior more closely simulates a liquid state, and, as will be shown in Sec. 9-10, an increase in temperature results in a decrease in viscosity. Finally, at very high-reduced temperatures, a condition again results in which pressure has little effect and viscosities increase with temperature.

The temperature–pressure region in Fig. 9-4 where viscosity changes rapidly with pressure is the very region where density also changes rapidly with pressure. Figure 9-7 shows a plot of the residual viscosity as a function of density for *n*-butane. A smooth curve results even though values over a range of temperatures are shown. This suggests that density is an important variable when describing viscosity behavior at high pressures, and several of the correlations presented in this section take advantage of this importance.

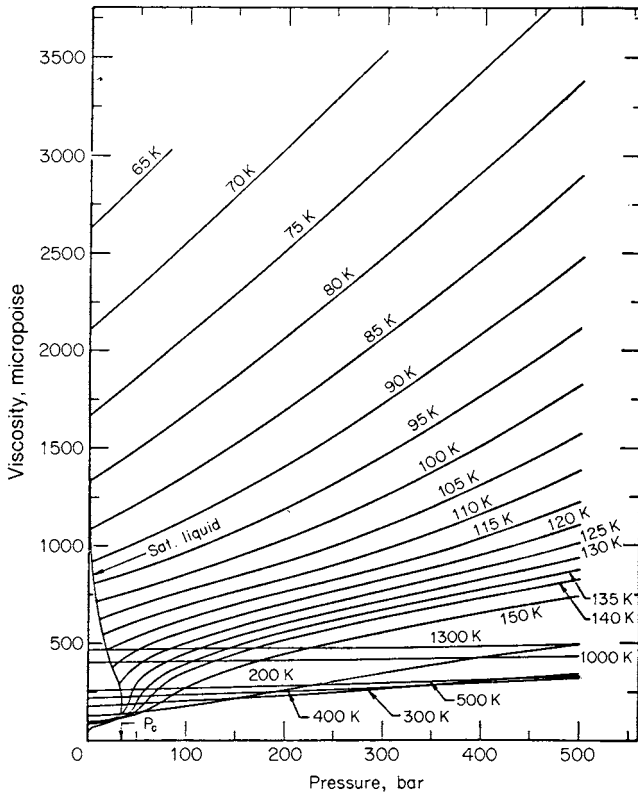


FIGURE 9-5 Viscosity of nitrogen. (Stephan and Lucas, 1979)

Enskog Dense-gas Theory

One of the very few theoretical efforts to predict the effect of pressure on the viscosity of gases is due to Enskog and is treated in detail by Chapman and Cowling (1939). The theory has also been applied to dense gas diffusion coefficients, bulk viscosities, and, for monatomic gases, thermal conductivities. The assumption is made that the gas consists of dense, hard spheres and behaves like a low-density hard-sphere system except that all events occur at a faster rate due to the higher rates of collision (Alder, 1966; Alder and Dymond, 1966). The increase in collision rate is proportional to the radial distribution function Ψ . The Enskog equation for shear viscosity is

$$\frac{\eta}{\eta^o} = \Psi^{-1} + 0.8 b_o \rho + 0.761 \Psi (b_o \rho)^2 \quad (9-6.1)$$

where η = viscosity, μP

η^o = low-pressure viscosity, μP

b_o = excluded volume = $\frac{2}{3} \pi N_o \sigma^3$, cm^3/mol

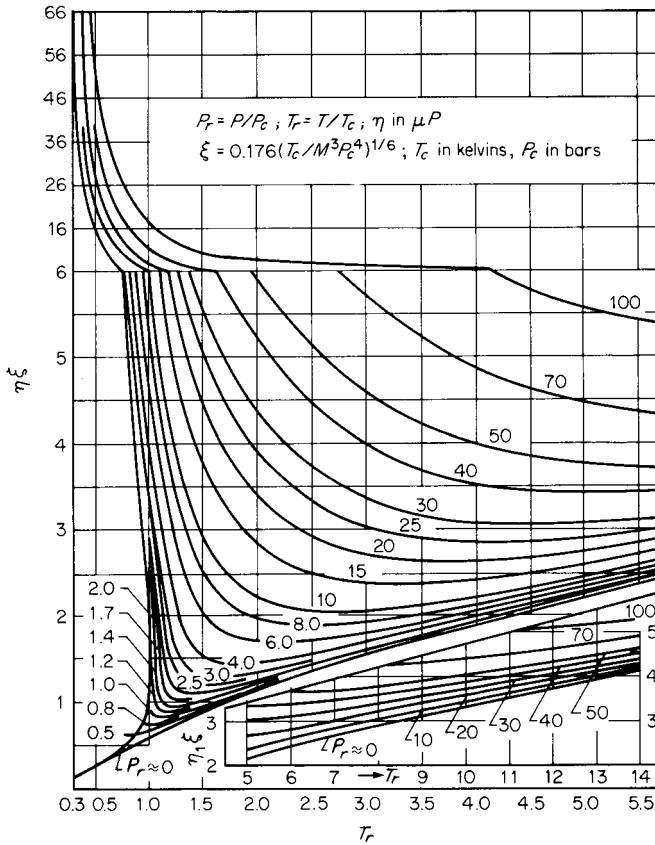


FIGURE 9-6 Generalized phase diagram for gas viscosity. (Lucas, 1981, 1983)

N_o = Avogadro's number
 σ = hard-sphere diameter, Å
 ρ = molar density, mole/cm³

Ψ is the radial distribution function at contact and can be related to an equation of state by

$$\Psi = \frac{Z - 1}{\rho b_o} \quad (9-6.2)$$

where Z is the compressibility factor.

Dymond among others (Assael, et al., 1996; Dymond and Assael, 1996) has continued efforts to modify the hard sphere approach in order to predict transport properties and has shown that viscosities of dense fluids can be correlated by the universal equation

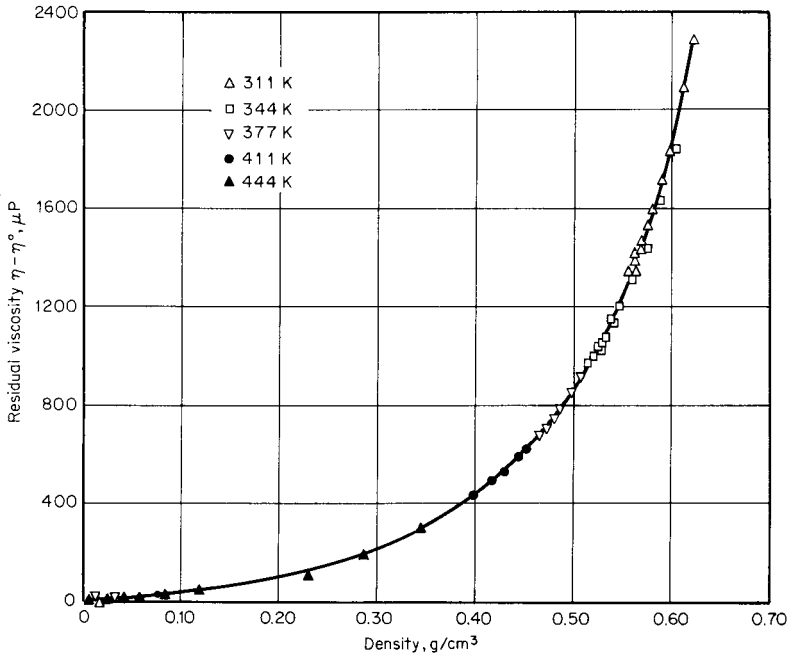


FIGURE 9-7 Residual *n*-butane viscosity as a function of density. (Dolan et al., 1963)

$$\log_{10} \eta_r = 1.0945 - \frac{9.26324}{V_r} + \frac{71.038}{V_r^2} - \frac{301.9012}{V_r^3} + \frac{797.69}{V_r^4} - \frac{1221.977}{V_r^5} + \frac{987.5574}{V_r^6} - \frac{319.4636}{V_r^7} \quad (9-6.3)$$

where $V_r = V/V_o$ and V_o is a close-packed volume. η_r is a reduced viscosity defined by

$$\eta_r = 6.619 \times 10^5 \frac{\eta V^{2/3}}{R_\eta (MT)^{1/2}} \quad (9-6.4)$$

where η is in Pa·s, V is in cm³/mol, M is g/mol and T is in K. R_η is a parameter that accounts for deviations from smooth hard spheres. The two parameters, V_o and R_η are compound specific and are not functions of density. V_o is a function of temperature as is R_η for *n*-alcohols (Assael, et al., 1994). For *n*-alkanes (Assael, et al., 1992a, 1992b), aromatic hydrocarbons (Assael, et al., 1992c), refrigerants (Assael, et al., 1995), and a number of other compounds (Assael, et al. 1992; Bleazard and Teja, 1996), R_η has been found to be independent of temperature. In theory, the two parameters V_o and R_η could be set with two experimental viscosity-density data, but in practice, Eq. (9-6.3) has been used only for systems for which extensive data are available. It has been applied to densities above the critical density and applicability to temperatures down to $T_r \approx 0.6$ has been claimed. Values of V_o and

R_η at 298 K and 350 K (as well as R_λ which is discussed in Chap. 10) for 16 fluids have been calculated with equations given in the above references and are shown in Table 9-5.

Xiang, et al. (1999) have recently extended Eq. (9-6.1) to cover the entire fluid range by introducing a crossover function between the low pressure limit and the high pressure limit. With a single equation, they fit low pressure viscosities to within 4% and liquid and high pressure viscosities generally to within 10% for 18 pure fluids. Their equation requires the density, critical properties, the acentric factor and values for σ and ε/k .

Reichenberg Method (1971, 1975, 1979)

In this case, the viscosity ratio η/η^o is given by Eq. (9-6.5)

$$\frac{\eta}{\eta^o} = 1 + Q \frac{AP_r^{3/2}}{BP_r + (1 + CP_r^D)^{-1}} \quad (9-6.5)$$

The constants, A , B , C , and D are functions of the reduced temperature T_r as shown below, and η^o is the viscosity of the gas at the same T and low pressure.

$$A = \frac{\alpha_1}{T_r} \exp \alpha_2 T_r^a \quad B = A(\beta_1 T_r - \beta_2)$$

$$C = \frac{\gamma_1}{T_r} \exp \gamma_2 T_r^c \quad D = \frac{\delta_1}{T_r} \exp \delta_2 T_r^d$$

TABLE 9-5 Typical values of V_o , R_η , and R_λ .

	V_o , cm ³ /mol		R_η		R_λ	
	298 K	350 K	298 K	350 K	298 K	350 K
Methane	17.9	17.3	1.00	1.00	1.16	1.16
<i>n</i> -Butane	84.1	84.3	1.08	1.08	1.67	1.67
<i>n</i> -Decane	134.3	130.1	1.53	1.53	3.13	3.13
Cyclohexane	77.4	75.7	0.93	0.93	1.35	1.35
CCl ₄	65.4	63.8	1.07	1.07	1.57	1.57
R134a	43.7	41.7	1.10	1.10	1.61	1.82
Ethanol	33.8	32.7	4.62	2.80	1.42	1.42
<i>n</i> -Hexanol	91.9	84.4	3.00	3.00	1.95	1.95
Acetic acid	41.3	41.2	0.76	0.76	0.92	0.98
Butyl ethanoate	89.8	88.3	1.10	1.10	2.20	2.25
2-Ethoxyethanol	70.7	68.0	1.33	1.33	1.65	1.78
1,3-Propanediol	62.2	59.1	1.04	1.04	1.16	1.32
Diethylene glycol	78.1	73.6	1.83	1.83	1.65	1.94
Diethanolamine	87.9	80.6	2.38	2.38	1.37	1.72
Triethylamine	73.8	66.4	2.48	2.48	3.03	3.47
Dimethyl disulfide	58.3	57.0	1.12	1.12	1.79	1.79

$$\begin{array}{llll} \alpha_1 = 1.9824 \times 10^{-3} & \alpha_2 = 5.2683 & a = -0.5767 & \beta_1 = 1.6552 \\ \beta_2 = 1.2760 & \gamma_1 = 0.1319 & \gamma_2 = 3.7035 & c = -79.8678 \\ \delta_1 = 2.9496 & \delta_2 = 2.9190 & d = -16.6169 & \end{array}$$

and $Q = (1 - 5.655 \mu_r)$, where μ_r is defined in Eq. (9-4.17). For nonpolar materials, $Q = 1.0$. Example 9-9 illustrates the application of Eq. (9-6.5), and, in Table 9-7, experimental dense gas viscosities are compared to the viscosities estimated with this method. Errors are generally only a few percent; the poor results for ammonia at 420 K seem to be an anomaly.

Example 9-9 Use Reichenberg's method to estimate the viscosity of *n*-pentane vapor at 500 K and 101 bar. The experimental value is 546 μP (Stephan and Lucas, 1979).

solution Whereas one could estimate the low-pressure viscosity of *n*-pentane at 500 K by using the methods described in Sec. 9-4, the experimental value is available (114 μP) (Stephan and Lucas, 1979) and will be used. The dipole moment of *n*-pentane is zero, so $Q = 1.0$. From Appendix A, $T_c = 469.7$ K and $P_c = 33.7$ bar. Thus $T_r = (500/469.7) = 1.065$ and $P_r = (101/33.7) = 3.00$. From the definitions of A , B , C , and D given under Eq. (9-6.5), $A = 0.2999$, $B = 0.1458$, $C = 1.271$, and $D = 7.785$. With Eq. (9-6.5),

$$\begin{aligned} \frac{\eta}{\eta^*} &= 1 + \frac{(0.2999)(3.00)^{3/2}}{(0.1458)(3.00) + [1 + (1.271)(3.00)^{7.785}]^{-1}} = 4.56 \\ \eta &= (4.56)(114) = 520 \mu\text{P} \\ \text{Error} &= \frac{520 - 546}{546} \times 100 = -4.7\% \end{aligned}$$

If one refers back to Fig. 9-6, at $T_r = 1.065$ and $P_r = 3.00$, the viscosity is changing rapidly with both temperature and pressure. Thus, an error of only 5% is quite remarkable.

Lucas (1980, 1981, 1983) Method

In a technique which, in some aspects, is similar to Reichenberg's, Lucas (1980, 1981, 1983) recommends the following procedure. For the reduced temperature of interest, first calculate a parameter Z_1 with Eq. (9-6.6).

$$\begin{aligned} Z_1 = \eta^0 \xi &= [0.807 T_r^{0.618} - 0.357 \exp(-0.449 T_r) \\ &\quad + 0.340 \exp(-4.058 T_r) + 0.018] F_P^\alpha F_Q^\alpha \end{aligned} \quad (9-6.6)$$

where η^0 refers to the low-pressure viscosity. Next calculate Z_2 . If $T_r \leq 1.0$ and $P_r < (P_{vp}/P_c)$, then

$$Z_2 = 0.600 + 0.760 P_r^\alpha + (6.990 P_r^\beta - 0.6)(1 - T_r) \quad (9-6.7)$$

$$\begin{aligned} \text{with } \alpha &= 3.262 + 14.98 P_r^{5.508} \\ \beta &= 1.390 + 5.746 P_r \end{aligned}$$

If $(1 < T_r < 40)$ and $(0 < P_r \leq 100)$, then

$$Z_2 = \eta^o \xi \left[1 + \frac{aP_r^e}{bP_r^f + (1 + cP_r^d)^{-1}} \right] \quad (9-6.8)$$

where $\eta^o \xi$ is found from Eq. (9-6.6). The term multiplying this group is identical to the pressure correction term in Reichenberg's method, Eq. (9-6.5), but the values of the constants are different.

$$a = \frac{a_1}{T_r} \exp \alpha_2 T_r^\gamma$$

$$b = a(b_1 T_r - b_2)$$

$$c = \frac{c_1}{T_r} \exp c_2 T_r^\delta$$

$$d = \frac{d_1}{T_r} \exp d_2 T_r^\epsilon$$

$$e = 1.3088$$

$$f = f_1 \exp f_2 T_r^\zeta$$

$$\text{and } a_1 = 1.245 \times 10^{-3} \quad a_2 = 5.1726 \quad \gamma = -0.3286$$

$$b_1 = 1.6553 \quad b_2 = 1.2723$$

$$c_1 = 0.4489 \quad c_2 = 3.0578 \quad \delta = -37.7332$$

$$d_1 = 1.7368 \quad d_2 = 2.2310 \quad \epsilon = -7.6351$$

$$f_1 = 0.9425 \quad f_2 = -0.1853 \quad \zeta = 0.4489$$

After computing Z_1 and Z_2 , we define

$$Y = \frac{Z_2}{Z_1} \quad (9-6.9)$$

and the correction factors F_p and F_Q ,

$$F_p = \frac{1 + (F_p^o - 1)Y^{-3}}{F_p^o} \quad (9-6.10)$$

$$F_Q = \frac{1 + (F_Q^o - 1)[Y^{-1} - (0.007)(\ln Y)^4]}{F_Q^o} \quad (9-6.11)$$

where F_p^o and F_Q^o are low-pressure polarity and quantum factors determined as shown in Eqs. (9-4.18) and (9-4.19). Finally, the dense gas viscosity is calculated as

$$\eta = \frac{Z_2 F_p F_Q}{\xi} \quad (9-6.12)$$

where ξ is defined in Eq. (9-4.15). At low pressures, Y is essentially unity, and $F_p = 1$, $F_Q = 1$. Also Z_2 then equals $\eta^o \xi$ so $\eta \rightarrow \eta^o$, as expected.

The Lucas method is illustrated in Example 9-10, and calculated dense gas viscosities are compared with experimental data in Table 9-7. In Example 9-10 and Table 9-7, the low-pressure viscosity η^o was not obtained from experimental data, but was estimated by the Lucas method in Sec. 9-4. Except in a few cases, the error was found to be less than 5%. The critical temperature, critical pressure, critical compressibility factor, and dipole moment are required, as well as the system temperature and pressure.

Example 9-10 Estimate the viscosity of ammonia gas at 420 K and 300 bar by using Lucas's method. The experimental values of η and η^o are 571 and 146 μP (Stephan and Lucas, 1979).

solution For ammonia we use $M = 17.031$, $Z_c = 0.244$, $T_c = 405.50$ K, $P_c = 113.53$ bar, and $\mu = 1.47$ debyes. Thus, $T_r = (420/405.50) = 1.036$ and $P_r = (300/113.53) = 2.643$. From Eq. (9-4.15),

$$\xi = (0.176) \left[\frac{405.50}{(17.031)^3 (113.53)^4} \right]^{1/6} = 4.95 \times 10^{-3} (\mu\text{P})^{-1}$$

with Eq. (9-4.17),

$$\mu_r = (52.46) \left[\frac{(1.47)^2 (113.53)}{(405.50)^2} \right] = 7.827 \times 10^{-2}$$

$$F_Q^o = 1.0$$

and with Eq. (9-4.18),

$$F_P^o = 1 + 30.55(0.292 - 0.244)^{1.72} |0.96 + (0.1)(1.036 - 0.7)| = 1.164$$

From Eq. (9-6.6), $Z_1 = \eta^o \xi = 0.7259$

$$\eta^o = \frac{0.7258}{4.96 \times 10^{-3}} = 147 \mu\text{P}$$

$$\text{Error} = \frac{147 - 146}{146} \times 100 = 0.7\%$$

The estimation of the low-pressure viscosity of ammonia agrees very well with the experimental value.

Since $T_r > 1.0$, we use Eq. (9-6.8) to determine Z_2 . The values of the coefficients are $a = 0.1998$, $b = 8.834 \times 10^{-2}$, $c = 0.9764$, $d = 9.235$, $e = 1.3088$, and $f = 0.7808$. Then,

$$\begin{aligned} Z_2 &= \left\{ 1 + \frac{(0.1998)(2.643)^{1.3088}}{(8.834 \times 10^{-2})(2.643)^{0.7808} + [1 + (0.9764)(2.643)^{9.235}]^{-1}} \right\} (0.7259) \\ &= (4.776)(0.7258) \\ &= 3.466 \end{aligned}$$

with Eqs. (9-6.9) to (9-6.11),

$$Y = \frac{3.466}{0.7258} = 4.775$$

$$F_P = \frac{1 + (1.164 - 1)(4.775)^{-3}}{1.164} = 0.860$$

$$F_Q = 1.0$$

and, with Eq. (9-6.12),

$$\eta = \frac{(3.466)(0.860)(1.0)}{4.96 \times 10^{-3}} = 602 \mu\text{P}$$

$$\text{Error} = \frac{602 - 571}{571} \times 100 = 5.4\%$$

The Reichenberg and Lucas methods employ temperature and pressure as the state variables. In most other dense gas viscosity correlations, however, the temperature and density (or specific volume) are used. In those cases, one must have accurate volumetric data or an applicable equation of state to determine the dense gas viscosity. Three different methods are illustrated below.

Method of Jossi, Stiel, and Thodos (Jossi, et al., 1962; Stiel and Thodos, 1964)

In this case, the residual viscosity $\eta - \eta^\circ$ is correlated with fluid density. All temperature effects are incorporated in the η° term. To illustrate the behavior of the $\eta - \eta^\circ$ function, consider Fig. 9-7, which shows $\eta - \eta^\circ$ for *n*-butane graphed as a function of density (Dolan, et al., 1963). Note that there does not appear to be any specific effect of temperature over the range shown. At the highest density, 0.6 g/cm³, the reduced density ρ/ρ_c is 2.63. Similar plots for many other substances are available, for example, He, air, O₂, N₂, CH₄ (Kestin and Leidenfrost, 1959); ammonia (Carmichael, et al., 1963; Shimotake and Thodos, 1963); rare gases (Shimotake and Thodos, 1958); diatomic gases (Brebach and Thodos, 1958); sulfur dioxide (Shimotake and Thodos, 1963a); CO₂ (Kennedy and Thodos, 1961; Vesovic, et al., 1990); steam (Kestin and Moszynski, 1959); and various hydrocarbons (Carmichael and Sage, 1963; Eakin and Ellington, 1963; Giddings, 1963; Starling, et al., 1960; Starling and Ellington, 1964). Other authors have also shown the applicability of a residual viscosity-density correlation (Golubev, 1959; Hanley, et al., 1969; Kestin and Moszynski, 1959; Rogers and Brickwedde, 1965; Starling, 1960, 1962).

In the Jossi, Stiel, and Thodos method, separate residual viscosity expressions are given for nonpolar and polar gases, but no quantitative criterion is presented to distinguish these classes.

Nonpolar Gases (Jossi, et al., 1962)

The basic relation is

$$[(\eta - \eta^\circ)\xi_T + 1]^{1/4} = 1.0230 + 0.23364 \rho_r + 0.58533 \rho_r^2 - 0.40758 \rho_r^3 + 0.093324 \rho_r^4 \quad (9-6.13)$$

where η = dense gas viscosity, μP

η^o = low-pressure gas viscosity, μP

ρ_r = reduced gas density, $\rho/\rho_c = V_c/V$

ξ_T = the group $(T_c/M^3 P_c^4)^{1/6}$, where T_c is in kelvins and P_c is in atmospheres, $(\mu\text{P})^{-1}$

M = molecular weight, g/mol

This relation is reported by Jossi, et al. to be applicable in the range $0.1 \leq \rho_r < 3$.

Polar Gases (Stiel and Thodos, 1964)

The relation to be used depends on the reduced density:

$$(\eta - \eta^o)\xi_T = 1.656\rho_r^{1.111} \quad \rho_r \leq 0.1 \quad (9-6.14)$$

$$(\eta - \eta^o)\xi_T = 0.0607(9.045\rho_r + 0.63)^{1.739} \quad 0.1 \leq \rho_r \leq 0.9 \quad (9-6.15)$$

$$\log\{4 - \log[(\eta - \eta^o)\xi_T]\} = 0.6439 - 0.1005\rho_r - \Delta \quad 0.9 \leq \rho_r < 2.6 \quad (9-6.16)$$

where $\Delta = 0$ when $0.9 \leq \rho_r \leq 2.2$ and

$$\Delta = (4.75 \times 10^{-4})(\rho_r^3 - 10.65)^2 \quad \text{when } 2.2 < \rho_r < 2.6 \quad (9-6.17)$$

and $(\eta - \eta^o)\xi_T = 90.0$ and 250 at $\rho_r = 2.8$ and 3.0 , respectively. The notation used in Eqs. (9-6.14) to (9-6.17) is defined under Eq. (9-6.13). Note that the parameter ξ_T is *not* the same as ξ defined earlier in Eq. (9-4.15).

An example of the Jossi, et al. method is shown below, and calculated dense gas viscosities are compared with experimental values in Table 9-7.

Example 9-11 Use the Jossi, Stiel, and Thodos method to estimate the viscosity of isobutane at 500 K and 100 bar. The experimental viscosity is $261 \mu\text{P}$ (Stephan and Lucas, 1979) and the specific volume is $243.8 \text{ cm}^3/\text{mol}$ (Waxman and Gallagher, 1983). At low pressure and 500 K, $\eta^o = 120 \mu\text{P}$.

solution Since isobutane is nonpolar, Eq. (9-6.13) is used. From Appendix A, $T_c = 407.85 \text{ K}$, $P_c = 36.4 \text{ bar} = 35.9 \text{ atm}$, $V_c = 262.7 \text{ cm}^3/\text{mol}$, and $M = 58.123$. Then

$$\xi_T = \left[\frac{(407.85)}{(58.123)^3(35.9)^4} \right]^{1/6} = 3.282 \times 10^{-2}(\mu\text{P})^{-1}$$

The reduced density $= \rho_r = V_c/V = 262.7/243.8 = 1.078$. With Eq. (9-6.13)

$$\begin{aligned} [(\eta - 120)(3.282 \times 10^{-2}) + 1]^{1/4} &= 1.0230 + (0.23364)(1.078) \\ &\quad + (0.58533)(1.078)^2 \\ &\quad - (0.40758)(1.078)^3 \\ &\quad + (0.093324)(1.078)^4 \\ &= 1.571 \end{aligned}$$

$$\eta = 275 \mu\text{P}$$

$$\text{Error} = \frac{275 - 261}{261} \times 100 = 5.4\%$$

Chung, et al. Method (1988)

In an extension of the Chung, et al. technique to estimate low-pressure gas viscosities, the authors began with Eq. (9-3.9) and employed empirical correction factors to account for the fact that the fluid has a high density. Their relations are shown below.

$$\eta = \eta^* \frac{36.344(MT_c)^{1/2}}{V_c^{2/3}} \quad (9-6.18)$$

where η = viscosity, μP

M = molecular weight, g/mol

T_c = critical temperature, K

V_c = critical volume, cm^3/mol

and

$$\eta^* = \frac{(T^*)^{1/2}}{\Omega_v} \{ F_c[(G_2)^{-1} + E_6 y] \} + \eta^{**} \quad (9-6.19)$$

T^* and F_c are defined as in Eqs. (9-4.9) and (9-4.11). Ω_v is found with Eq. (9-4.3) as a function of T^* , and, with ρ in mol/cm^3 ,

$$y = \frac{\rho V_c}{6} \quad (9-6.20)$$

$$G_1 = \frac{1 - 0.5 y}{(1 - y)^3} \quad (9-6.21)$$

$$G_2 = \frac{E_1 \{ [1 - \exp(-E_4 y)]/y \} + E_2 G_1 \exp(E_5 y) + E_3 G_1}{E_1 E_4 + E_2 + E_3} \quad (9-6.22)$$

$$\eta^{**} = E_7 y^2 G_2 \exp[E_8 + E_9 (T^*)^{-1} + E_{10} (T^*)^{-2}] \quad (9-6.23)$$

and the parameters E_1 to E_{10} are given in Table 9-6 as linear functions of ω (the acentric factor), μ_r^4 [as defined in Eq. (9-4.12)], and the association factor κ (see Table 9-1). One might note that, at very low densities, y approaches zero, G_1 and G_2 approach unity, and η^{**} is negligible. At these limiting conditions, combining

TABLE 9-6 Chung, et al. Coefficients to Calculate $E_i = a_i + b_i \omega + c_i \mu_r^4 + d_i \kappa$

i	a_i	b_i	c_i	d_i
1	6.324	50.412	-51.680	1189.0
2	1.210×10^{-3}	-1.154×10^{-3}	-6.257×10^{-3}	0.03728
3	5.283	254.209	-168.48	3898.0
4	6.623	38.096	-8.464	31.42
5	19.745	7.630	-14.354	31.53
6	-1.900	-12.537	4.985	-18.15
7	24.275	3.450	-11.291	69.35
8	0.7972	1.117	0.01235	-4.117
9	-0.2382	0.06770	-0.8163	4.025
10	0.06863	0.3479	0.5926	-0.727

Eqs. (9-6.18), (9-6.19) and (9-4.9) leads to Eq. (9-4.10), which then applies for estimating η° .

The application of the Chung, et al. method is shown in Example 9-12. Some calculated values of η are compared with experimental results in Table 9-7. The agreement is quite good and errors usually are below 5%.

Example 9-12 With the Chung, et al. method, estimate the viscosity of ammonia at 520 K and 600 bar. The experimental value of η is 466 μP (Stephan and Lucas, 1979). At this temperature, $\eta^\circ = 182 \mu\text{P}$. The specific volume of ammonia at 520 K and 600 bar is 48.2 cm^3/mol (Haar and Gallagher, 1978).

solution We use $T_c = 405.50 \text{ K}$, $V_c = 72.4 \text{ cm}^3/\text{mol}$, $\omega = 0.256$, $M = 17.031$, and $\mu = 1.47$ debyes. Thus $T_r = 520/405.50 = 1.282$ and $\rho = 1/48.2 = 2.07 \times 10^{-2} \text{ mol/cm}^3$.

With Eq. (9-4.12),

$$\mu_r = \frac{(131.3)(1.47)}{[(72.4)(405.50)]^{1/2}} = 1.13$$

and with Eq. (9-4.11),

$$F_c = 1 - (0.2756)(0.256) + (0.059035)(1.13)^4 = 1.026$$

$$T^* = (1.2593)(1.282) = 1.615$$

and with Eq. (9-4.3), $\Omega_v = 1.275$. Using Eqs. (9-6.20) and (9-6.21),

$$y = \frac{(2.075 \times 10^{-2})(72.4)}{6} = 0.250 \text{ and } G_1 = 2.074$$

From Table 9-6, the following coefficients were computed: $E_1 = -65.03$, $E_2 = -9.287 \times 10^{-3}$, $E_3 = -204.3$, $E_4 = 2.575$, $E_5 = -1.706$, $E_6 = 3.018$, $E_7 = 6.749$, $E_8 = 1.103$, $E_9 = -1.552$, and $E_{10} = 1.124$. Then, with Eq. (9-6.22), $G_2 = 1.472$ and, from Eq. (9-6.23), $\eta^{**} = 1.101$. Finally, using Eqs. (9-6.19) and (9-6.18),

$$\eta^* = \frac{(1.615)^{1/2}}{1.275} (1.026)[(1.472)^{-1} + (3.018)(0.250)] + 1.101 = 2.567$$

$$\eta = \frac{(2.567)(36.344)[(17.031)(405.50)]^{1/2}}{(72.4)^{2/3}} = 446 \mu\text{P}$$

$$\text{Error} = \frac{446 - 466}{466} \times 100 = -4.2\%$$

TRAPP Method (Huber, 1996)

The TRAPP (transport property prediction) method is a corresponding states method to calculate viscosities and thermal conductivities of pure fluids and mixtures. In its original version (Ely, 1981; Ely and Hanel, 1981), it was also used to estimate low pressure values of λ and η and employed methane as a reference fluid. In the most recent version presented below for pure fluids and later in Sec. 9-7 for mixtures, low pressure values are estimated by one of the methods presented earlier in the chapter, propane is the reference fluid, and shape factors are no longer

TABLE 9-7 Comparison of Experimental and Calculated Dense Gas Viscosities

Compound	T , K	P , bar	V , cm ³ mole	Ref.*	η , μP	η° , μP	Reichenberg, Eq. (9-6.5)	Lucas, Eq. (9-6.12)	Jossi, et al., Eq. (9-6.13)	Chung, et al., Eq. (9-6.18) Table 9-6	Brulé and Starling, Eq. (9-6.18) Table 9-8	Trapp
Oxygen	300	30.4	806.1	6	212.8	207.2	-1.0	-1.6	0.6	-1.5	0.2	-0.2
		81.0	295.3		225.7		-1.2	-1.1	-0.6	-1.9	0.8	-0.4
		152.0	155.3		250.3		-0.3	-0.2	-0.8	-0.2	1.6	-0.3
		304.0	81.4		319.3		3.6	0.8	2.8	3.9	4.6	0.6
Methane	200	40.0	282.0	3	90	78.0	7.0	0.6	5.9	3.5	1.7	6.8
		100.0	60.2		296		10.0	8.2	5.1	3.1	14	7.8
		200.0	51.1		415		3.8	5.0	-0.5	-2.2	16	8.1
		500										
Isobutane	500	40	1039.0	3	180	177	-0.4	-5.6	0.9	-5.3	-3.8	0.1
		100	417.7		187		-0.6	-5.1	0.3	-7.2	-2.3	0.0
		200	213.7		204		-1.0	-5.0	-0.3	-2.9	-1.0	-1.0
		500	98.9		263		1.5	-3.3	3.3	2.5	5.3	-1.1
Isobutane	500	20	2396.0	7	127	120	0.9	6.3	0.2	0.8	2.2	-0.3
		50	620.0		146		5.7	12.0	4.5	9.3	12	5.9
		100	244.0		261		-5.2	3.8	5.4	5.5	8.6	2.3
		200	159.0		506		-11	2.3	-9.0	-7.2	-5.0	-6.1
Ammonia	420	400	130.0	4	794		-19	-8.2	-16	-10	-9.9	-11
		50	588.1		149	146	3.0	-2.4	1.7	3.1	-5.2	4.9
		150	61.9		349		-17	-6.5	-15	-13	5.1	14
		300	39.8		571		-21	5.2	3.6	-4.0	22	60
Ammonia	520	600	34.3	4	752		-24	7.8	11	-1.3	31	84
		50	807.6		185	182	0.7	-5.8	0.5	-0.1	-9.2	2.0
		150	229.6		196		4.5	0.9	2.3	4.0	1.6	9.4
		300	90.7		296		-1.4	5.3	-2.3	0.7	13	5.0
	600		48.2		466		-13	5.8	-3.2	-3.4	12	36

Carbon dioxide	360	50	514.6	1	190	177	3.0	3.1	1.9	1.1	2.4	2.6
		100	211.2		230		2.1	3.3	0.8	3.6	6.1	1.2
		400	55.0		730		1.3	7.7	-3.5	-0.8	1.2	6.3
		800	45.8		1104		-7.0	1.1	-9.6	-2.2	-1.3	4.0
<i>n</i> -Pentane	500	50	802.8	1	243	235	0.0	3.0	1.3	0.7	1.6	0.7
		100	389.2		254		1.7	5.1	1.4	3.3	5.3	2.0
		400	97.1		411		9.8	7.4	2.6	3.6	9.4	2.1
		800	62.9		636		10	9.6	0.9	-3.2	2.8	3.0
<i>n</i> -Pentane	600	20.3	2240	2	143	134	0.0	1.4	0.0	1.2	2.1	0.2
		81.1	418.3		242		-7.5	-5.3	-11	-4.6	-1.0	-8.5
		152	237.5		383		0.9	2.3	-7.9	-7.0	-3.7	-1.3

[†]Percent error = [(calc. - exp.)/exp.] × 100.

*References: 1, Angus, et al. (1976); 2, Das, et al. (1977); 3, Goodwin (1973); 4, Haar and Gallagher (1978); 5, Stephan and Lucas (1979); 6, Stewart (1966). Ideal gas values from Stephan and Lucas (1979).

functions of density. Other reference fluids could be chosen and in fact, Huber and Ely (1992) use R134a as the reference fluid to describe the viscosity behavior of refrigerants. The TRAPP method was originally developed only for nonpolar compounds, but there have been efforts to extend the method to polar compounds as well (Hwang and Whiting, 1987).

In the TRAPP method, the residual viscosity of a pure fluid is related to the residual viscosity of the reference fluid, propane:

$$\eta - \eta^o = F_\eta[\eta^R - \eta^{Ro}] \quad (9-6.24)$$

The reference fluid values are evaluated at T_o and density ρ_o , not T and ρ . In Eq. (9-6.24), η^o is the viscosity at low pressure. η^R is the true viscosity of the reference fluid, propane, at temperature T_o and density ρ_o . η^{Ro} is the low pressure value for propane at temperature T_o . For propane Younglove and Ely (Zaytsev and Aseyev, 1992) give

$$\eta^R - \eta^{Ro} = G_1 \exp[\rho_o^{0.1} G_2 + \rho_o^{0.5} (\rho_r^R - 1) G_3] - G_1 \quad (9-6.25)$$

where $\rho_r^R = \rho_o / \rho_c^R$, $\eta^R - \eta^{Ro}$ is in $\mu\text{Pa}\cdot\text{s}$, and

$$G_1 = \exp(E_1 + E_2/T) \quad (9-6.26)$$

$$G_2 = E_3 + E_4/T^{1.5} \quad (9-6.27)$$

$$G_3 = E_5 + \frac{E_6}{T} + \frac{E_7}{T^2} \quad (9-6.28)$$

$$E_1 = -14.113294896$$

$$E_2 = 968.22940153$$

$$E_3 = 13.686545032$$

$$E_4 = -12511.628378$$

$$E_5 = 0.0168910864$$

$$E_6 = 43.527109444$$

$$E_7 = 7659.4543472$$

T_o , ρ_o , and F_η are calculated by

$$T_o = T/f \quad (9-6.29)$$

$$\rho_o = \rho h \quad (9-6.30)$$

$$F_\eta = \left(\frac{M}{44.094} f \right)^{1/2} h^{-2/3} \quad (9-6.31)$$

where f and h are equivalent substance reducing ratios and are determined as described below.

If vapor pressure and liquid density information are available for the substance of interest, and if $T < T_c$, it is recommended that f be obtained from the equation

$$\frac{P_{vp}}{\rho^S} = f \frac{P_{vp}^R(T_o)}{\rho^{SR}(T_o)} \quad (9-6.32)$$

where P_{vp} and ρ^S are the vapor pressure and saturated liquid density at temperature, T . $P_{vp}^R(T_o)$ and $\rho^{SR}(T_o)$ are for the reference fluid, propane. Because the density and vapor pressure of the reference fluid are evaluated at $T_o = T/f$, Eq. (9-6.32) must be solved iteratively. Once f is found from Eq. (9-6.32), h is determined from

$$h = \rho^{SR}(T_o)/\rho^S \quad (9-6.33)$$

If $T > T_c$, or if vapor pressure and saturated liquid density information are not available, h and f can be calculated by

$$f = \frac{T_c}{T_c^R} [1 + (\omega - \omega^R)(0.05203 - 0.7498 \ln T_r)] \quad (9-6.34)$$

$$h = \frac{\rho_c^R}{\rho_c} \frac{Z_c^R}{Z_c} [1 - (\omega - \omega^R)(0.1436 - 0.2822 \ln T_r)] \quad (9-6.35)$$

The application of the TRAPP method is shown in Example 9-13. Some calculated values of η are compared with experimental results in Table 9-7. Huber (1996) gives results of additional comparisons and also suggests methods to improve predictions if some experimental data are available.

Example 9-13 Repeat Example 9-11 with the TRAPP method.

solution From Appendix A, for the reference fluid, propane, $T_c = 369.83$ K, $V_c = 200$ cm³/mol, $Z_c = 0.276$ and $\omega = 0.152$. For isobutane, $T_c = 407.85$ K, $V_c = 259$ cm³/mol, $Z_c = 0.278$ and $\omega = 0.186$. With Eqs. (9-6.34) and (9-6.35) followed by Eqs. (9-6.29) to (9-6.31)

$$f = \frac{407.85}{369.83} [1 + (0.186 - 0.152)(0.05203 - 0.7498 \ln(1.226))] = 1.099$$

$$h = \frac{259 \times 0.276}{200 \times 0.278} [1 - (0.186 - 0.152)(0.1436 - 0.2882 \ln(1.226))] = 1.282$$

$$T_o = 500/1.099 = 454.9 \text{ K}, \quad \rho_o = 1.282/243.8 = 0.005258 \text{ mol/cm}^3$$

$$F_\eta = \left(\frac{58.124 \times 1.099}{44.094} \right)^{1/2} (1.282)^{-2/3} = 1.020$$

For the T_o and ρ_o above, Eqs. (9-6.25) to (9-6.28) give $\eta^R - \eta^{Ro} = 14.41$ $\mu\text{Pa s} = 144.1$ μP Eq. (9-6.24) gives

$$\eta = 120 + 1.020 \times 144.1 = 267.0 \text{ } \mu\text{P}$$

$$\text{Error} = \frac{267 - 261}{261} \times 100 = 2.3\%$$

Other Corresponding States Methods

In a manner identical in form with that of Chung, et al., Brulé and Starling (1984) proposed a different set of coefficients for E_1 to E_{10} to be used instead of those in

Table 9-6. These are shown in Table 9-8. Note that no polarity terms are included and the *orientation* parameter γ has replaced the acentric factor ω . If values of γ are not available, the acentric factor may be substituted.

The Brulé and Starling technique was developed to be more applicable for heavy hydrocarbons rather than for simple molecules as tested in Table 9-7.

Okeson and Rowley (1991) have developed a four-parameter corresponding-states method for polar compounds at high pressures, but did not test their method for mixtures.

Discussion and Recommendations for Estimating Dense Gas Viscosities

Six estimation techniques were discussed in this section. Two (Reichenberg and Lucas) were developed to use temperature and pressure as the input variables to estimate the viscosity. The other four require temperature and density; thus, an equation of state would normally be required to obtain the necessary volumetric data if not directly available. In systems developed to estimate many types of properties, it would not be difficult to couple the *PVT* and viscosity programs to provide densities when needed. In fact, the Brulé and Starling method (Brulé and Starling, 1984) is predicated on combining thermodynamic and transport analyses to obtain the characterization parameters most suitable for both types of estimations.

Another difference to be recognized among the methods noted in this section is that Reichenberg's, Jossi, et al.'s and the TRAPP methods require a low-pressure viscosity at the same temperature. The other techniques bypass this requirement and have imbedded into the methods a low-pressure estimation method; i.e., at low densities they reduce to techniques as described in Sec. 9-4. If the Lucas, Chung, et al., or Brulé-Starling method were selected, no special low-pressure estimation method would have to be included in a property estimation package.

With these few remarks, along with the testing in Table 9-7 as well as evaluations by authors of the methods, we recommend that either the Lucas or Chung, et al. procedure be used to estimate dense (and dilute) gas viscosities of both polar and nonpolar compounds. The Brulé-Starling method is, however, preferable when com-

TABLE 9-8 Brulé and Starling Coefficients
to Calculate $E_i = a_i + b_i\gamma$

i	a_i	b_i
1	17.450	34.063
2	-9.611×10^{-4}	7.235×10^{-3}
3	51.043	169.46
4	-0.6059	71.174
5	21.382	-2.110
6	4.668	-39.941
7	3.762	56.623
8	1.004	3.140
9	-7.774×10^{-2}	-3.584
10	0.3175	1.1600

Note: If γ values are not available, use ω , the acentric factor, or, preferably, obtain from multi-property analysis by using vapor pressure data. (Brulé and Starling, 1984)

plex hydrocarbons are of interest, but even for those materials, the Chung, et al. procedure should be used at low reduced temperatures ($T_r < 0.5$). For nonpolar compounds, we recommend the TRAPP method as well as the Lucas or Chung, et al. methods.

Except when one is working in temperature and pressure ranges in which viscosities are strong functions of these variables (See Fig. 9-6), errors for the recommended methods are usually only a few percent. Near the critical point and in regions where the fluid density is approaching that of a liquid, higher errors may be encountered.

9-7 VISCOSITY OF GAS MIXTURES AT HIGH PRESSURES

The most convenient method to estimate the viscosity of dense gas mixtures is to combine, where possible, techniques given previously in Secs. 9-5 and 9-6.

Lucas Approach (Lucas 1980, 1981, 1983)

In the (pure) dense gas viscosity approach suggested by Lucas, Eqs. (9-6.6) to (9-6.12) were used. To apply this technique to mixtures, rules must be chosen to obtain T_c , P_c , M , and μ as functions of composition. For T_c , P_c , and M of the mixture, Eqs. (9-5.18) to (9-5.20) should be used. The polarity (and quantum) corrections are introduced by using Eqs. (9-6.10) and (9-6.11), where F_p^o and F_Q^o refer to mixture values from Eqs. (9-5.21) and (9-5.22). The parameter Y in Eqs. (9-6.10) and (9-6.11) must be based on T_{cm} and P_{cm} . F_p^o and F_Q^o , for the pure components, were defined in Eqs. (9-4.18) and (9-4.19).

Chung, et al. (1988) Approach

To use this method for dense gas mixtures, Eqs. (9-6.18) to (9-6.23) are used. The parameters T_c , V_c , ω , M , μ and κ in these equations are given as functions of composition in Sec. 9-5. That is,

Parameter	Equations to use
T_{cm}	(9-5.44), (9-5.27)
V_{cm}	(9-5.43), (9-5.25)
ω_m	(9-5.29), (9-5.25)
V_{cm}	(9-5.32), (9-5.33), (9-5.25) and (9-5.43)
μ_m	(9-5.30), (9-5.25)
κ_m	(9-5.31)

TRAPP Method (Huber, 1996)

For gas mixtures at high pressure, the viscosity is determined by a combination of the techniques introduced for high-pressure gases (Sec. 9-6) with appropriate mixing rules. The viscosity of the mixture is given by:

$$\eta_m - \eta_m^o = F_{\eta m}[\eta^R - \eta^{Ro}] + \Delta\eta^{\text{ENSKOG}} \quad (9-7.1)$$

The quantity $\eta^R - \eta^{Ro}$ that appears in Eq. (9-7.1) is for the reference fluid propane and is evaluated with Eq. (9-6.25) at T_o and ρ_o . The following mixing rules are used to determine $F_{\eta m}$, T_o and ρ_o .

$$h_m = \sum_i \sum_j y_i y_j h_{ij} \quad (9-7.2)$$

$$f_m h_m = \sum_i \sum_j y_i y_j f_{ij} h_{ij} \quad (9-7.3)$$

$$h_{ij} = \frac{[(h_i)^{1/3} + (h_j)^{1/3}]^3}{8} \quad (9-7.4)$$

$$f_{ij} = (f_i f_j)^{1/2} \quad (9-7.5)$$

f_i and h_i are determined as in Sec. 9-6. T_o and ρ_o are calculated by equations similar to Eqs. (9-6.29) and (9-6.30):

$$T_o = T/f_m \quad (9-7.6)$$

$$\rho_o = \rho h_m = h_m/V \quad (9-7.7)$$

Finally,

$$F_{\eta m} = (44.094)^{-1/2} (h_m)^{-2} \sum_i \sum_j y_i y_j (f_{ij} M_{ij})^{1/2} (h_{ij})^{4/3} \quad (9-7.8)$$

where

$$M_{ij} = \frac{2 M_i M_j}{M_i + M_j} \quad (9-7.9)$$

The term, $\Delta\eta^{\text{ENSKOG}}$, accounts for size differences (Ely, 1981) and is calculated by

$$\Delta\eta^{\text{ENSKOG}} = \eta_m^{\text{ENSKOG}} - \eta_x^{\text{ENSKOG}} \quad (9-7.10)$$

where

$$\eta_m^{\text{ENSKOG}} = \sum_i \beta_i Y_i + \alpha \rho^2 \sum_i \sum_j y_i y_j \sigma_{ij}^6 \eta_{ij}^o g_{ij} \quad (9-7.11)$$

ρ = density in mols/L, σ is in Å, and η^o and η^{ENSKOG} are in μP

$$\alpha = \frac{48}{25\pi} \left[\frac{2\pi}{3} (6.023 \times 10^{-4}) \right]^2 = 9.725 \times 10^{-7} \quad (9-7.12)$$

$$\sigma_i = 4.771 h_i^{1/3} \quad (9-7.12)$$

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (9-7.13)$$

Because $\Delta\eta^{\text{ENSKOG}}$ is a correction based on a hard sphere assumption, Eq. (9-3.8) is used to calculate η^o . The radial distribution function, g_{ij} , is calculated (Tham and Gubbins, 1971) by

$$g_{ij} = (1 - \xi)^{-1} + \frac{3\xi}{(1 - \xi)^2} \Theta_{ij} + \frac{2\xi^2}{(1 - \xi)^3} \Theta_{ij}^2 \quad (9-7.14)$$

$$\Theta_{ij} = \frac{\sigma_i \sigma_j \sum_k y_k \sigma_k^2}{2\sigma_{ij} \sum_k y_k \sigma_k^3} \quad (9-7.15)$$

$$\xi = (6.023 \times 10^{-4}) \frac{\pi}{6} \rho \sum_i y_i \sigma_i^3 \quad (9-7.16)$$

$$Y_i = y_i \left[1 + \frac{8\pi}{15} (6.023 \times 10^{-4}) \rho \sum_j y_j \left(\frac{M_j}{M_i + M_j} \right) \sigma_{ij}^3 g_{ij} \right] \quad (9-7.17)$$

The n values of β_i are obtained by solving the n linear equations of the form

$$\sum_j B_{ij} \beta_j = Y_i \quad (9-7.18)$$

where

$$B_{ij} = 2 \sum_k y_i y_k \frac{g_{ik}}{\eta_{ik}^o} \left(\frac{M_k}{M_i + M_k} \right)^2 \left[\left(1 + \frac{5 M_i}{3 M_k} \right) \delta_{ij} - \frac{2 M_i}{3 M_k} \delta_{jk} \right] \quad (9-7.19)$$

In Eq. (9-7.19), δ_{ij} is the Kronecker delta function, 1 if $i = j$, and 0 if $i \neq j$. The quantity η_x^{ENSKOG} that appears in Eq. (9-7.10) is for a pure hypothetical fluid with the same density as the mixture and is determined with Eq. (9-7.11) with σ_x defined by

$$\sigma_x = \left(\sum_i \sum_j y_i y_j \sigma_{ij}^3 \right)^{1/3} \quad (9-7.20)$$

$$M_x = \left[\sum_i \sum_j y_i y_j M_{ij}^{1/2} \sigma_{ij}^4 \right]^2 \sigma_x^{-8} \quad (9-7.21)$$

M_{ij} and σ_{ij} are defined in Eqs. (9-7.9) and (9-7.13). Huber (1996) tested the TRAPP method on a number of binary hydrocarbon mixtures over a wide range of densities and reports an average absolute error of about 5%, although, in some cases, significantly larger deviations were found. The method is illustrated in Example 9-14.

Example 9-14 Use the TRAPP method to estimate the viscosity of a mixture of 80 mol % methane (1) and 20 mol % n -decane at 377.6 K and 413.7 bar. Lee, et al. (1966) report at these conditions, $\rho = 0.4484 \text{ g/cm}^3$ and $\eta_{\text{exp}} = 126 \mu\text{Pa} \cdot \text{s}$, although this value is considerably higher than values reported by Knapstad, et al. (1990) at similar conditions.

solution From Appendix A

	M	T_c, K	$V_c, \text{cm}^3/\text{mol}$	Z_c	ω
CH ₄	16.043	190.56	98.6	0.286	0.011
C ₁₀ H ₂₂	142.285	617.7	624	0.256	0.490

Using Eqs. (9-7.2) to (9-7.9) and the procedure illustrated in Example 10-8 leads to $f_m = 0.9819$, $h_m = 0.8664$, $T_o = 384.6$ K, $\rho_o = 9.408$ mol/L, and $\eta^R - \eta^{Ro} = 51.72$ $\mu\text{Pa} \cdot \text{s}$. Equation (9-7.8) gives $F_{\eta m} = 1.260$. Calculation of $\Delta\eta^{\text{ENSKOG}}$ requires the application of the method described in Eqs. (9-7.10) through (9-7.21). Intermediate results include $\rho = 10.86$ mol/L, $\xi = 0.3668$ with other values shown below:

ij	$\sigma_{ij}, \text{\AA}$	$\eta_{ij}^o, \mu \text{ Pa} \cdot \text{s}$	g_{ij}	$B_{ij} \times 10^4$
11	3.716	15.0	2.696	210.7
12	5.314	9.86	3.085	-6.076
22	6.913	13.0	3.873	28.18

When $Y_1 = 2.014$ and $Y_2 = 0.5627$ are used in Eq. (9-7.18), this equation is written for each of the two components and solved to give $\beta_1 = 102.0$ and $\beta_2 = 221.6$. Finally, Eq. (9-7.11) gives $\eta_m^{\text{ENSKOG}} = 911$ μP . From Eqs. (9-7.20) and (9-7.21), $\sigma_x = 4.548$ \AA and $M_x = 47.50$. Then, for the hypothetical pure fluid, Eq. (9-7.16) gives

$$\xi = 6.023 \times 10^{-4} \frac{\pi}{6} (10.86)(4.548)^3 = 0.3222$$

Eq. (9-7.14), with $\Theta_{xx} = 1/2$, gives

$$g_{xx} = \frac{1}{1 - 0.3222} + \frac{1}{2} \frac{3 \times 0.3222}{(1 - 0.3222)^2} + \frac{2(0.3222)^2}{(1 - 0.3222)^3} \frac{1}{4} = 2.694$$

Eq. (9-7.17) gives

$$Y_x = 1 + \frac{8\pi}{15} (6.023 \times 10^{-4})(10.86) \frac{(4.548)^3(2.694)}{2} = 2.389$$

From Eq. (9-3.8)

$$\eta_x^o = 26.69 \frac{(47.50 \times 377.6)^{1/2}}{(4.548)^2} = 172.8 \mu\text{P}$$

For a pure component, Eq. (9-7.19) reduces to $B_{xx} = g_{xx}/\eta_x^o$, so that $B_{xx} = 2.694/172.8 = 0.01559$. Then Eq. (9-7.18) gives $\beta_x = 2.389/0.01559 = 153.2$. Applying Eq. (9-7.11) to a pure fluid gives

$$\eta_x^{\text{ENSKOG}} = 153.2 \times 2.389 + 9.725 \times 10^{-7} (10.86)^2 (4.548)^6 (172.8)(2.694) = 839 \mu\text{P}$$

With Eq. (9-7.10)

$$\Delta\eta^{\text{ENSKOG}} = 911 - 839 = 72 \mu\text{P} = 7.2 \mu\text{Pa} \cdot \text{s}.$$

Then using Eq. (9-7.1)

$$\eta_m = 10.2 + 1.260 \times 51.72 + 7.2 = 82.6 \mu\text{Pa} \cdot \text{s}.$$

$$\text{Error} = \frac{82.6 - 126}{126} \times 100 = -34\%$$

In the above example, for the low pressure contribution of 10.2 $\mu\text{Pa}\cdot\text{s}$, Eq. (9-3.9) was used for methane, (9-4.16) was used for decane, and (9-5.16) was used for the mixture. Although the TRAPP prediction in Example 9-14 was lower than the experimental value reported by Lee, et al. (1966), TRAPP predictions are considerably higher than the experimental values reported in (Knapstad, et al., 1990)

for the same system at similar conditions. High-quality data for mixtures with different size molecules at high pressures are limited. This in turn limits the ability to evaluate models for this case.

Discussion

Both the Lucas and Chung, et al. methods use the relations for the estimation of dense gas viscosity and apply a one-fluid approximation to relate the component parameters to composition. The TRAPP method uses the term $\Delta\eta^{\text{ENSKOG}}$ to improve the one-fluid approximation. In the Lucas method, the state variables are T , P , and composition, whereas in the TRAPP and Chung, et al. procedures, T , ρ , and composition are used.

The accuracy of the Lucas and Chung, et al. forms is somewhat less than when applied to pure, dense gases. Also, as noted at the end of Sec. 9-6, the accuracy is often poor when working in the critical region or at densities approaching those of a liquid at the same temperature. The TRAPP procedure can be extended into the liquid region. The paucity of accurate high-pressure gas mixture viscosity data has limited the testing that could be done, but Chung, et al. (1988) report absolute average deviations of 8 to 9% for both polar and nonpolar dense gas mixtures. A comparable error would be expected from the Lucas form. The TRAPP method gives similar deviations for nonpolar mixtures, but has not been tested for polar mixtures. Tilly, et al. (1994) recommended a variation of the TRAPP method to correlate viscosities of supercritical fluid mixtures in which various solutes were dissolved in supercritical carbon dioxide.

As a final comment to the first half of this chapter, it should be noted that, if one were planning a property estimation system for use on a computer, it is recommended that the Lucas, Chung, et al., or Brulé and Starling method be used in the dense gas mixture viscosity correlations. Then, at low pressures or for pure components, the relations simplify directly to those described in Secs. 9-4 to 9-6. In other words, it is not necessary, when using these particular methods, to program separate relations for low-pressure pure gases, low-pressure gas mixtures, and high-pressure pure gases. One program is sufficient to cover all those cases as well as high-pressure gas mixtures.

9-8 LIQUID VISCOSITY

Most gas and gas mixture estimation techniques for viscosity are modifications of theoretical expressions described briefly in Secs. 9-3 and 9-5. There is no comparable theoretical basis for the estimation of liquid viscosities. Thus, it is particularly desirable to determine liquid viscosities from experimental data when such data exist. Viswanath and Natarajan (1989) have published a compilation of liquid viscosity data for over 900 compounds and list constants that correlate these data. Liquid viscosity data can also be found in Gammon, et al. (1993–1998), Riddick, et al. (1986), Stephan and Lucas (1979), Stephen and Hildwein (1987), Stephan and Heckenberger (1988), Timmermans (1965), and Vargaftik, et al. (1996). Data for aqueous electrolyte solutions may be found in Kestin and Shankland (1981), Lobo (1990), and Zaytsev and Aseyev (1992). Tabulations of constants have been published in Daubert, et al. (1997), Duhne (1979), van Velzen et al. (1972), Yaws,

et al. (1976), and Yaws (1995, 1995a) that allow estimations of liquid viscosities. When these constants are derived from experimental data they can be used with confidence, but sometimes (Yaws, 1995, 1995a) they are based on estimated viscosities, and in such instances, they should be used only with caution. Liquid phase viscosity values can also be found in Dean (1999), Lide (1999), and Perry and Green (1997).

The viscosities of liquids are larger than those of gases at the same temperature. As an example, in Fig. 9-8, the viscosities of liquid and vapor benzene are plotted as functions of temperature. Near the normal boiling point (353.4 K), the liquid viscosity is about 36 times the vapor viscosity, and at lower temperatures, this ratio increases even further. Two vapor viscosities are shown in Fig. 9-8. The low-pressure gas line would correspond to vapor at about 1 bar. As noted earlier in Eq. (9-4.20), below T_c , low-pressure gas viscosities vary in a nearly linear manner with temperature. The curve noted as saturated vapor reflects the effect of the increase in vapor pressure at higher temperatures. The viscosity of the saturated vapor should equal that of the saturated liquid at the critical temperature (for benzene, $T_c = 562.0$ K).

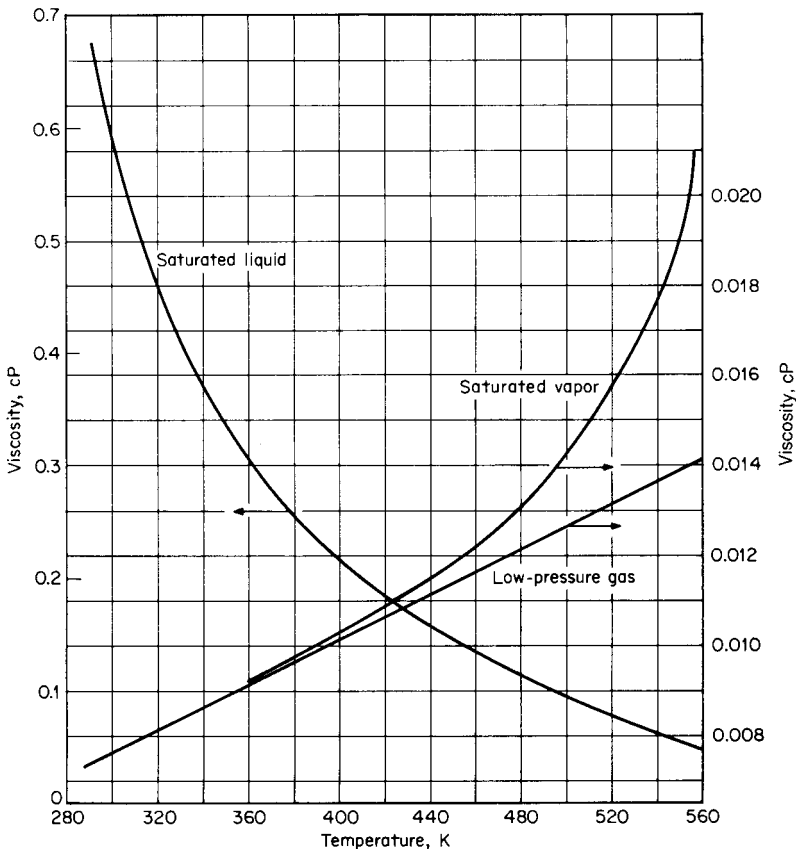


FIGURE 9-8 Viscosities of liquid and vapor benzene. ($T_b = 353.2$ K; $T_c = 562.0$ K).

Much of the curvature in the liquid viscosity-temperature curve may be eliminated if the logarithm of the viscosity is plotted as a function of reciprocal (absolute) temperature. This change is illustrated in Fig. 9-9 for four saturated liquids: ethanol, benzene, *n*-heptane, and nitrogen. (To allow for variations in the temperature range, the reciprocal of the reduced temperature is employed.) Typically, the normal boiling point would be at a value of $T_r^{-1} \approx 1.5$. For temperatures below the normal boiling point ($T_r^{-1} > 1.5$), the logarithm of the viscosity varies linearly with T_r^{-1} . Above the normal boiling point, this no longer holds. In the nonlinear region, several corresponding states estimation methods have been suggested, and they are covered in Sec. 9-12. In the linear region, most corresponding states methods have not been found to be accurate, and many estimation techniques employ a group contribution approach to emphasize the effects of the chemical structure on viscosity. The curves in Fig. 9-9 suggest that, at comparable reduced temperatures, viscosities of polar fluids are higher than those of nonpolar liquids such as hydrocarbons, which themselves are larger than those of simple molecules such as nitrogen. If one attempts to replot Fig. 9-9 by using a nondimensional viscosity such as $\eta\xi$ [see, for example, Eqs. (9-4.13) to (9-4.15)] as a function of T_r , the separation between curves diminishes, especially at $T_r > 0.7$. However, at lower values of T_r , there are still significant differences between the example compounds.

In the use of viscosity in engineering calculations, one is often interested not in the dynamic viscosity, but, rather, in the ratio of the dynamic viscosity to the density. This quantity, called the *kinematic viscosity*, would normally be expressed

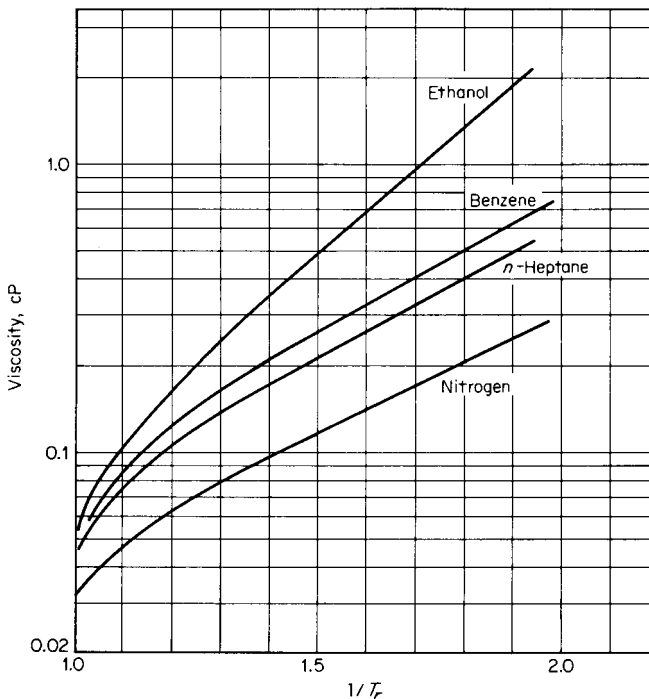


FIGURE 9-9 Viscosities of various liquids as functions of temperature. (Stephan and Lucas, 1979)

in m^2/s or in stokes. One stoke (St) is equivalent to $10^{-4} \text{ m}^2/\text{s}$. The kinematic viscosity ν , decreases with increasing temperature in a manner such that $\ln \nu$ is nearly linear in temperature for both the saturated liquid and vapor as illustrated in Fig. 9-10 for benzene. As with the dynamic viscosity, the kinematic viscosities of the saturated vapor and liquid become equal at the critical point.

The behavior of the kinematic viscosity with temperature has led to several correlation schemes to estimate ν rather than η . However, in most instances, $\ln \nu$ is related to T^{-1} rather than T . If Fig. 9-10 is replotted by using T^{-1} , again there is a nearly linear correlation with some curvature near the critical point (as there is in Fig. 9-9).

In summary, pure liquid viscosities at high reduced temperatures are usually correlated with some variation of the law of corresponding states (Sec. 9-12). At lower temperatures, most methods are empirical and involve a group contribution approach (Sec. 9-11). Current liquid *mixture* correlations are essentially mixing rules relating pure component viscosities to composition (Sec. 9-13). Little theory has been shown to be applicable to estimating liquid viscosities (Andrade, 1954; Brokaw, et al., 1965; Brush, 1962; Gemant, 1941; Hirschfelder, et al., 1954).

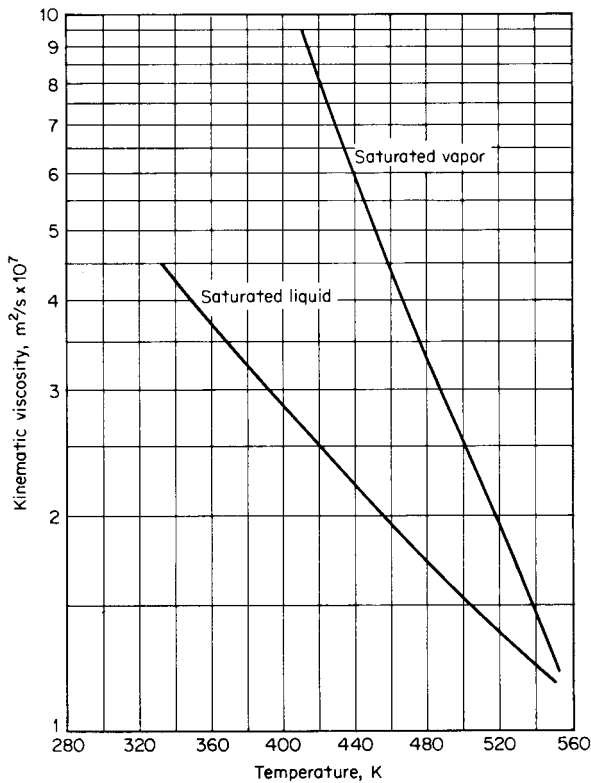


FIGURE 9-10 Kinematic viscosities of saturated liquid and vapor benzene ($T_b = 353.2 \text{ K}$; $T_c = 562.0 \text{ K}$).

9-9 EFFECT OF HIGH PRESSURE ON LIQUID VISCOSITY

Increasing the pressure over a liquid results in an increase in viscosity. Lucas (1981) has suggested that the change may be estimated from Eq. (9-9.1)

$$\frac{\eta}{\eta_{SL}} = \frac{1 + D(\Delta P_r/2.118)^A}{1 + C\omega\Delta P_r} \quad (9-9.1)$$

where η = viscosity of the liquid at pressure P

η_{SL} = viscosity of the saturated liquid at P_{vp}

$\Delta P_r = (P - P_{vp})/P_c$

ω = acentric factor

$A = 0.9991 - [4.674 \times 10^{-4}/(1.0523T_r^{-0.03877} - 1.0513)]$

$D = [0.3257/(1.0039 - T_r^{2.573})^{0.2906}] - 0.2086$

$C = -0.07921 + 2.1616T_r - 13.4040T_r^2 + 44.1706T_r^3 - 84.8291T_r^4 + 96.1209T_r^5 - 59.8127T_r^6 + 15.6719T_r^7$

In a test with 55 liquids, polar and nonpolar, Lucas found errors in the calculated viscosities of less than 10%. To illustrate the predicted values of Eq. (9.9.1), Figs. 9-11 and 9-12 were prepared. In both, η/η_{SL} was plotted as a function of ΔP_r for various reduced temperatures. In Fig. 9-11, $\omega = 0$, and in Fig. 9-12, $\omega = 0.2$. Except at high values of T_r , η/η_{SL} is approximately proportional to ΔP_r . The effect of pressure is more important at the high reduced temperatures. As the acentric factor increases, there is a somewhat smaller effect of pressure. The method is illustrated in Example 9-15.

Example 9-15 Estimate the viscosity of liquid methylcyclohexane at 300 K and 500 bar. The viscosity of the saturated liquid at 300 K is 0.68 cP, and the vapor pressure is less than 1 bar.

solution From Appendix A, $T_c = 572.19$ K, $P_c = 34.71$ bar, and $\omega = 0.235$. Thus $T_r = 300/572.19 = 0.524$ and $\Delta P_r = 500/34.71 = 14.4$. (P_{vp} was neglected.) Then

$$A = 0.9991 - \frac{4.674 \times 10^{-4}}{(1.0523)(0.524)^{-0.03877} - 1.0513} = 0.9822$$

$$D = \frac{0.3257}{[1.0039 - (0.524)^{2.573}]^{0.2906}} - 0.2086 = 0.1371$$

$$\begin{aligned} C &= -0.07921 + (2.1616)(0.524) - (13.4040)(0.524)^2 + (44.1706)(0.524)^3 \\ &\quad - (84.8291)(0.524)^4 + (96.1209)(0.524)^5 - (59.8127)(0.524)^6 \\ &\quad + (15.6719)(0.524)^7 = 0.0619 \end{aligned}$$

With Eq. (9-9.1),

$$\frac{\eta}{\eta_{SL}} = \frac{1 + (0.137)(14.4/2.118)^{0.9822}}{1 + (0.235)(14.4)(0.0619)} = 1.57$$

$$\eta = (1.57)(0.68) = 1.07 \text{ cP}$$

The experimental value of η at 300 K and 500 bar is 1.09 cP (Titani, 1929).

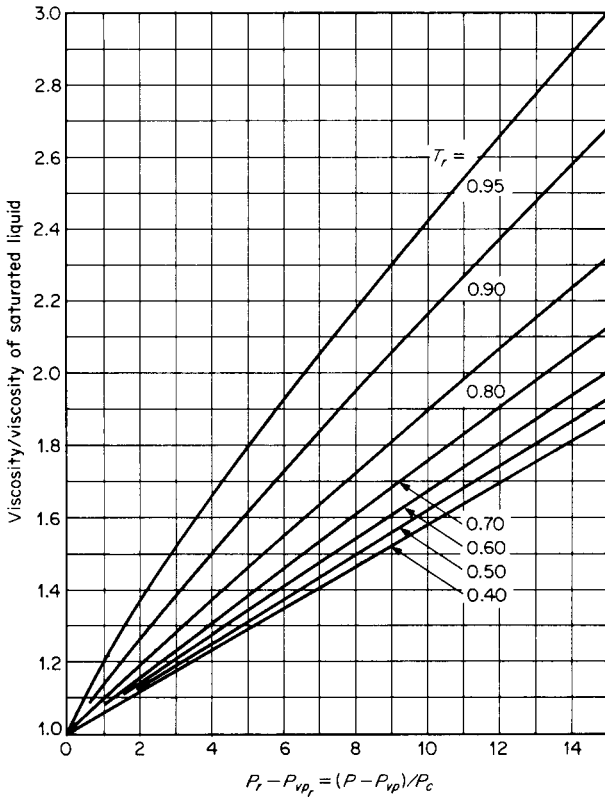


FIGURE 9-11 Effect of pressure on the viscosity of liquids $\omega = 0$.

$$\text{Error} = \frac{1.07 - 1.09}{1.09} \times 100 = -1.8\%$$

Whereas the correlation by Lucas would encompass most pressure ranges, at pressures over several thousand bar the data of Bridgman suggest that the logarithm of the viscosity is proportional to pressure and that the structural complexity of the molecule becomes important. Those who are interested in such high-pressure regions should consult the original publications of Bridgman (1926) or the work of Dymond and Assael (See Sec. 9.6, Assael, et al., 1996, or Dymond and Assael, 1996).

9-10 EFFECT OF TEMPERATURE ON LIQUID VISCOSITY

The viscosities of liquids decrease with increasing temperature either under isobaric conditions or as saturated liquids. This behavior can be seen in Fig. 9-9, where, for

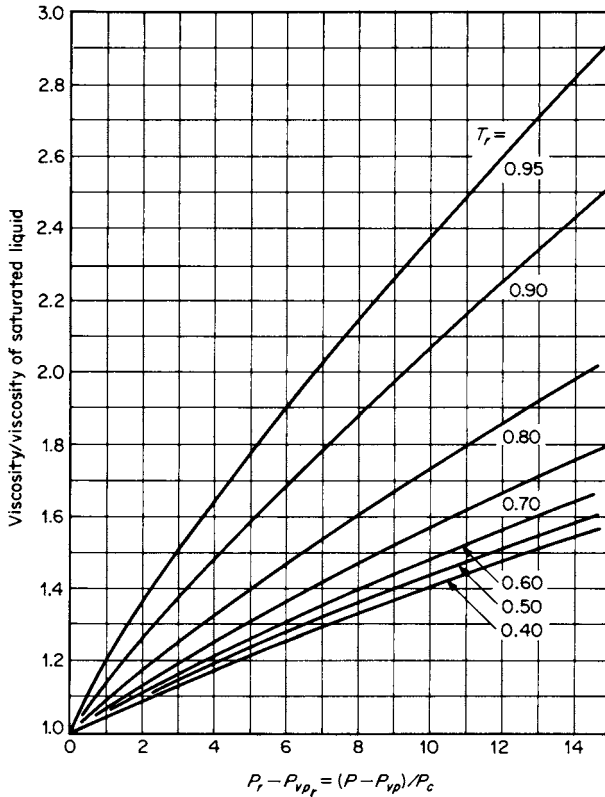


FIGURE 9-12 Effect of pressure on the viscosity of liquids; $\omega = 0.2$.

example, the viscosity of saturated liquid benzene is graphed as a function of temperature. Also, as noted in Sec. 9-8 and as illustrated in Fig. 9-10, for a temperature range from the freezing point to somewhere around the normal boiling temperature, it is often a good approximation to assume $\ln \eta_L$ is linear in reciprocal absolute temperature; i.e.,

$$\ln \eta_L = A + \frac{B}{T} \quad (9-10.1)$$

This simple form was apparently first proposed by de Guzman (1913) (O'Loane, 1979), but it is more commonly referred to as the Andrade equation (1930, 1934). Variations of Eq. (9-10.1) have been proposed to improve upon its correlation accuracy; many include some function of the liquid molar volume in either the A or B parameter (Bingham and Stookey, 1939; Cornelissen and Waterman, 1955; Eversteijn, et al., 1960; Girifalco, 1955; Gutman and Simmons, 1952; Innes, 1956; Marschalko and Barna, 1957; Medani and Hasan, 1977; Miller, 1963, 1963a; Telang, 1945; and van Wyk, et al., 1940). Another variation involves the use of a third constant to obtain the Vogel equation (1921),

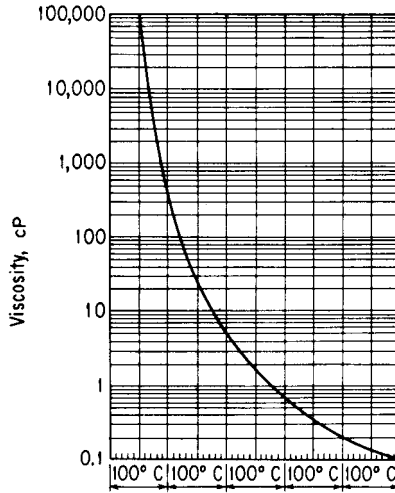


FIGURE 9-13 Lewis and Squires liquid viscosity-temperature correlation. (*Lewis and Squires, 1934 as adapted in Gambill, 1959*)

$$\ln \eta_L = A + \frac{B}{T + C} \quad (9-10.2)$$

Goletz and Tassios (1977) have used this form (for the kinematic viscosity) and report values of A , B , and C for many pure liquids.

Equation (9-10.1) requires at least two viscosity-temperature datum points to determine the two constants. If only one datum point is available, one of the few ways to extrapolate this value is to employ the approximate Lewis-Squires chart (1934), which is based on the empirical fact that the sensitivity of viscosity to temperature variations appears to depend primarily upon the value of the viscosity. This chart, shown in Fig. 9-13, can be used by locating the known value of viscosity on the ordinate and then extending the abscissa by the required number of degrees to find the new viscosity. Figure 9-13 can be expressed in an equation form as

$$\eta_L^{-0.2661} = \eta_K^{-0.2661} + \frac{T - T_K}{233} \quad (9-10.3)$$

where η_L = liquid viscosity at T , cP

η_K = known value of liquid viscosity at T_K , cP

T and T_K may be expressed in either °C or K. Thus, given a value of η_L at T_K , one can estimate values of η_L at other temperatures. Equation (9-10.3) or Fig. 9-13 is only approximate, and errors of 5 to 15% (or greater) may be expected. This method should not be used if the temperature is much above the normal boiling point.

Example 9-16 The viscosity of acetone at 30°C is 0.292 cP; estimate the viscosities at -90°C, -60°C, 0°C, and 60°C.

solution At -90°C , with Eq. (9-10.3),

$$\eta_L^{-0.2661} = (0.292)^{-0.2661} + \frac{-90 - 30}{233}$$

$$\eta_L = 1.7 \text{ cP}$$

For the other cases,

$T, ^{\circ}\text{C}$	$\eta_L, \text{ cP}$ Eq. (9-10.3)	$\eta_L, \text{ cP}$ Experimental	Percent error
-90	1.7	2.1	-19
-60	0.99	0.98	1
0	0.42	0.39	8
60	0.21	0.23	-9

In summary, from the freezing point to near the normal boiling point, Eq. (9-10.1) is a satisfactory temperature-liquid viscosity function. Two datum points are required. If only one datum point is known, a rough approximation of the viscosity at other temperatures can be obtained from Eq. (9-10.3) or Fig. 9-14.

Liquid viscosities above the normal boiling point are treated in Sec. 9-12.

9-11 ESTIMATION OF LOW-TEMPERATURE LIQUID VISCOSITY

Estimation methods for low-temperature liquid viscosity often employ structural-sensitive parameters which are valid only for certain homologous series or are found from group contributions. These methods usually use some variation of Eq. (9-10.1) and are limited to reduced temperatures less than about 0.75. We present two such methods in this section. We also describe a technique that employs corresponding states concepts. None of the three methods considered is particularly reliable.

Orrick and Erbar (1974) Method

This method employs a group contribution technique to estimate A and B in Eq. (9-11.1).

$$\ln \frac{\eta_L}{\rho_L M} = A + \frac{B}{T} \quad (9-11.1)$$

where η_L = liquid viscosity, cP
 ρ_L = liquid density at 20°C , g/cm^3
 M = molecular weight
 T = temperature, K

The group contributions for obtaining A and B are given in Table 9-9. For liquids that have a normal boiling point below 20°C , use the value of ρ_L at 20°C ; for liquids

TABLE 9-9 Orrick and Erbar (1974) Group Contributions for A and B in Eq. (9-11.1)

Group	A	B
Carbon atoms [†]	$-(6.95 + 0.21N)$	$275 + 99N$
$\begin{array}{c} \\ \text{R}-\text{C}-\text{R} \\ \\ \text{R} \end{array}$	-0.15	35
$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{C}-\text{R} \\ \\ \text{R} \end{array}$	-1.20	400
Double bond	0.24	-90
Five-membered ring	0.10	32
Six-membered ring	-0.45	250
Aromatic ring	0	20
Ortho substitution	-0.12	100
Meta substitution	0.05	-34
Para substitution	-0.01	-5
Chlorine	-0.61	220
Bromine	-1.25	365
Iodine	-1.75	400
-OH	-3.00	1600
-COO-	-1.00	420
-O-	-0.38	140
$\begin{array}{c} \\ -\text{C}=\text{O} \end{array}$	-0.50	350
-COOH	-0.90	770

[†] N = number of carbon atoms not including those in other groups shown above.

whose freezing point is above 20°C, ρ_L at the melting point should be employed. Compounds containing nitrogen or sulfur cannot be treated. Orrick and Erbar tested this method for 188 organic liquids. The errors varied widely, but they reported an average deviation of 15%. This is close to the average value of 16% shown in Table 9-11 for a more limited test. Since ρ_L in Eq. (9-11.1) is at 20°C and not T , the temperature of the liquid, Eq. (9-11.1) is the same form as the Andrade equation, Eq. (9-10.1).

Example 9-17 Estimate the viscosity of liquid n -butyl alcohol at 120°C with the Orrick-Erbar method. The experimental value is 0.394 cP.

solution From Table 9-9

$$A = -6.95 - (0.21)(4) - 3.00 = -10.79$$

$$B = 275 + (99)(4) + 1600 = 2271$$

From Vargaftik, et al. (1996), at 20°C, $\rho_L = 0.8096 \text{ g/cm}^3$ and $M = 74.123$. Then, with Eq. (9-11.1),

$$\ln \frac{\eta_L}{(0.8096)(74.123)} = -10.79 + \frac{2271}{T}$$

$$\text{At } T = 120^\circ\text{C} = 393 \text{ K}, \eta_L = 0.400 \text{ cP}$$

$$\text{Error} = \frac{0.400 - 0.394}{0.394} \times 100 = 1.5\%$$

Sastri-Rao Method (1992)

In this method, the pure liquid viscosity is calculated with the equation

$$\eta = \eta_B P_{vp}^{-N} \quad (9-11.2)$$

P_{vp} is the vapor pressure in atmospheres and η_B is the viscosity at the normal boiling point, T_b , in mPa·s. Below T_b , Sastri and Rao determine P_{vp} with the equation

$$\ln P_{vp} = (4.5398 + 1.0309 \ln T_b) \times \left(1 - \frac{(3 - 2T/T_b)^{0.19}}{T/T_b} - 0.38(3 - 2T/T_b)^{0.19} \ln(T/T_b) \right) \quad (9-11.3)$$

Equation (9-11.3) should be used only when $T < T_b$. Equation (9-11.3) is not necessarily the most accurate equation for vapor pressure predictions but should be used with Eq. (9-11.2) because the group contributions used to estimate η_B and N have been determined when P_{vp} was calculated with Eq. (9-11.3). η_B is determined with the equation

$$\eta_B = \sum \Delta\eta_B + \sum \Delta\eta_{Bcor} \quad (9-11.4)$$

N is determined from

$$N = 0.2 + \sum \Delta N + \sum \Delta N_{cor} \quad (9-11.5)$$

Values for group contributions to determine the summations in Eqs. (9-11.4) and (9-11.5) are given in Table 9-10. The contributions of the functional groups to η_B and N are generally cumulative. However, if the compound contains more than one identical functional group, its contributions for N should be taken only once unless otherwise mentioned. Thus for branched hydrocarbons with multiple $>\text{CH}-$ groups, N is 0.25. In Table 9-10, the term alicyclic means cycloparaffins and cycloolefins and excludes aromatics and heterocyclics. In the contributions of halogen groups, “others” means aromatics, alicyclics, and heterocyclics while the carbon groups listed are meant for aliphatic compounds. Also for halogens, the values of ΔN for aliphatic, alicyclics and aromatics are not used if other non-hydrocarbon groups are present in the cyclic compound (See footnote b in the halogen section of Table 9-10). For example, the corrections for halogenated pyridines and anilines are given in footnote b and are not to be used in conjunction with the corrections listed under “aliphatic, alicyclics and aromatics.” Calculation of η_B and N is illustrated in Example 9-18 and typical deviations are shown in Table 9-11.

Example 9-18 Determine the values of η_B and N to be used in Eq. (9-11.2) for o-xylene, ethanol, ethylbenzene, 2-3-dimethylbutane, and o-chlorophenol.

TABLE 9-10 Sastri and Rao (1992) Group Contributions for η_B and N in Eq. (9-11.2)

Hydrocarbon groups			
Group	$\Delta\eta_B$	ΔN	Remarks and examples
Non-ring			
$-\text{CH}_3$	0.105	0.000	For n -alkanes, n -alkenes or n -alkynes with $C > 8$ $\Delta N_{\text{cor}} = 0.050$
$>\text{CH}_2$	0.000	0.000	
$>\text{CH}-$	-0.110	0.050	(i) if both $>\text{CH}-$ and $>\text{C}<$ groups are present $\Delta N_{\text{cor}} = 0.050$ only
$>\text{C}<$	-0.180	0.100	(ii) ΔN values applicable only for aliphatic hydrocarbons and halogenated derivatives of aliphatic compounds (e.g. 2,2,4 trimethyl pentane, chloroform, bromal) in other cases $\Delta N = 0.000$
$=\text{CH}_2$	0.085	0.000	
$=\text{CH}-$	-0.005	0.000	
$=\text{C}<$	-0.100	0.000	
$\text{HC}\equiv\text{C}-$	-0.115	0.075	
Examples of ΔN values			
Ring			
$>\text{CH}_2$	0.060	0.000	
$>\text{CH}-$	-0.085	0.000	ΔN for 2-methyl propane 0.050
$>\text{C}<$	-0.180	0.000	2,3-dimethylbutane 0.050 (see text)
$-\text{CH}-$	0.040	0.000	2,2-dimethylpropane 0.100
$=\text{CH}-$	0.050	0.000	2,2,4,4-tetramethyl pentane 0.100
$=\text{C}<$	-0.100	0.000	2,2,4-trimethylpentane 0.050 (both $>\text{CH}-$ and $>\text{C}<$ present)
$=\text{C}<$	-0.120	0.000	$>\text{CH}-$ in chloroform 0.050 but in isopropylamine 0.000 and
$=\text{C}<$	-0.040	0.000	isopropylbenzene 0.000
$=\text{CH}-$	-0.065	0.000	

Contributions of ring structure and hydrocarbon chains to ΔN_{cor}		
Structure	ΔN_{cor}	Remarks and examples
All monocyclic and saturated polycyclic hydrocarbon rings (unsubstituted)	0.100	cyclopentane, benzene, or cis-decalhydronaphthalene
Methyl substituted compounds of the above	0.050	ethylcyclopentane, toluene
Monocyclic monoalkyl alicyclic hydrocarbons		
$1 < C_{br} \leq 5$	0.025	ethylcyclopentane, <i>n</i> -pentylcyclohexane
$C_{br} > 5$	0.050	<i>n</i> -hexylcyclopentane
Monocyclic multisubstituted alkyl alicyclic hydrocarbons	0.025	1,3,5-trimethylcyclohexane
Monoalkyl benzenes with $C_{br} > 1$	0.025	ethylbenzene
Bicyclic hydrocarbons partly or fully unsaturated	0.050	tetralin, diphenyl, diphenylmethane
Unsaturated tricyclic hydrocarbons	0.100	<i>p</i> -terphenyl, triphenylmethane
Correction for multiple substitution in aromatics by hydrocarbon groups		
ortho	0.050	<i>o</i> -xylene, <i>o</i> -nitrotoluene
meta and para	0.000	<i>p</i> -xylene
1,3,5	0.100	1,3,5-trimethylbenzene
1,2,4	0.050	1,2,4-trimethylbenzene
1,2,6	0.000	
$\Delta \eta_{Bcor}$ for multiple substitution in aromatics by hydrocarbon groups = 0.070		

TABLE 9-10 Sastri and Rao (1992) Group Contributions for η_B and N in Eq. (9-11.2) (*Continued*)

Contribution of halogen groups									
$\Delta\eta_B$ for halogen attached to carbon in									
Group	Aliphatic compounds					Others		ΔN^b in halogenated hydrocarbons with no other functional groups	
	$-\text{CH}_3$ or $>\text{CH}_2^a$	$>\text{CH}-$	$>\text{C}<^a$	$=\text{CH}-$	$=\text{C}<$			Alicyclics	Aromatics
$-\text{F}^c$	0.185	0.155	0.115	n.d.	n.d.	0.185		0.075	0.025
$-\text{Cl}^a$	0.185	0.170	0.170	0.180	0.150	0.170		0.075	0.025
$-\text{Br}$	0.240	0.235	0.235	0.240	0.210	0.210		0.075	0.025
$-\text{I}$	0.260	0.260	n.d.	n.d.	n.d.	0.260		0.075	0.025
^a Special configurations/function group structure combination									
(1) $\text{X}-(\text{CH}_2)_n-\text{X}$ where X is halogen					ΔN_{cor}	Remarks and examples			
					0.050	1,3-dichloropropane			
(2) $\text{Cl}-\text{C}-\text{Cl}$ where the C is in a ring					0.050	For each group, one correction in hexachlorocyclopentadiene			
^b Case of non-hydrocarbon group present in cyclic compounds									
(1) Halogen attached to ring carbons in compounds containing									
(A) $-\text{NH}_2$ or phenolic $-\text{OH}$									
(B) oxygen-containing groups other than OH									
(C) other non-oxygen functional groups									
(2) Halogen attached to non-hydrocarbon functional group									
^c Fluorine groups in perfluorocompounds									
Group	$\Delta\eta_B$								
Non-ring									
$-\text{CF}_3$	$\Delta N=0.150$ for all perfluoro n -compounds								
$>\text{CF}_2$	0.000								
$>\text{CF}-$	$\Delta N=0.200$ for all isocompounds								
Ring									
$-\text{CF}_2-$	0.145								
$>\text{CF}-$	$\Delta N=0.200$ for all cyclic compounds								
	-0.170								

Contribution of oxygen groups

Group	Structure	$\Delta\eta_B$	ΔN	Remarks
—O—	Non-ring attached to ring carbon	0.020	0.050	For multiple occurrence $\Delta\eta_{\text{Bcor}} = 0.050$ (1,3-dimethoxybenzene) In compounds containing —NH ₂ or phenolic OH group attached to ring carbon $\Delta N_{\text{cor}} = -0.050$ (<i>o</i> -anisidine, 2-methoxyphenol)
—O—	Ring (Single) (Multiple occurrence)	0.120	0.050	
—O—	Others	0.200 0.000	0.150 0.050	Combined value (dioxane, paraldehyde) (i) In aliphatic compounds containing —OH, special value for the combination $\Delta N = 0.100$ (2-methoxyethanol) (ii) $\Delta\eta_{\text{Bcor}}$ for multiple occurrence 0.05 (dimethoxymethane)
>CO	Non-ring attached to ring carbon	0.030	0.050	(i) In the cyclic compounds containing NH ₂ group (with or without other functional groups) special value $\Delta N -0.100$ for the combination (ethylanthranilate) (ii) In cyclic compounds containing >NH group $\Delta\eta_{\text{Bcor}} = 0.080$ (acetanilide)
>CO	Ring	0.055	0.100	(i) In cyclic compounds containing >NH group $\Delta\eta_{\text{Bcor}} = 0.100$ (ii) In compounds containing —O— group special value $\Delta N = 0.125$ for the combination
>CO	Others	0.030	0.025	(i) For aliphatic compounds containing —NH ₂ or >N— groups (acetamide) $\Delta\eta_{\text{Bcor}} = 0.080$ (ii) For cyclic compounds containing >NH group (acetanilide) $\Delta\eta_{\text{Bcor}} = 0.080$
—C(O) ₃ C— —CHO	Anhydride Aldehyde	0.060 0.140	0.050 0.050	(iii) In aliphatic compounds containing —OH special value for the combination, $\Delta N = 0.125$ (diacetonealcohol) In compounds containing —OH (phenolic) special value for the combination, $\Delta N = 0.075$ (salicylaldehyde)

TABLE 9-10 Sastri and Rao (1992) Group Contributions for η_B and N in Eq. (9-11.2) (*Continued*)

Contribution of oxygen groups				
Group	Structure	$\Delta\eta_B$	ΔN	Remarks
—COO—	Ester	0.040	0.050	(i) For multiple occurrence, $\Delta N = 0.100$ (dibutylphthalate) (ii) For —H in formates $\Delta\eta_B = 0.165$ (iii) In cyclic compounds containing NH_2 group, special value for the combination, $\Delta N = 0.100$ (ethylanthanilate) (iv) For aliphatic compounds containing — NH_2 or $>\text{N}$ —groups, $\Delta\eta_{\text{Bcor}} = 0.080$ (methylcarbamate)
—COOH	In aliphatics saturated unsaturated In aromatics	0.220 0.250 0.195	0.100 0.100 0.175	For $C = 3$ or 4 $\Delta N = 0.050$
Contribution of hydroxyl groups				
Structure	$\Delta\eta_B$	ΔN	Remarks	
—OH in aliphatics saturated primary	$0.615 - 0.092C + 0.004C^2 - 10^{-0.58C}$ for $C \leq 10$ 0.095 for $C > 10$	0.3 for $2 < C < 12$ 0.15 for others	(i) In compounds containing —O— group special value for the combination, $\Delta N = 0.100$ (2 methoxy ethanol) (ii) In compounds containing $>\text{NH}$ group, special value for the combination, $\Delta N = 0.300$ (aminoethyl ethanolamine)	
Primary branched	$0.615 - 0.092C + 0.004C^2 - 10^{-0.58C}$	0.375		
Secondary straight chain	$0.615 - 0.092C + 0.004C^2 - 10^{-0.58C}$	0.450 for $C \leq 5$ 0.300 for $C > 5$		
Secondary branched	$0.615 - 0.092C + 0.004C^2 - 10^{-0.58C}$	0.450 for $C \leq 8$ 0.300 for $C > 8$		
Tertiary saturated	$0.615 - 0.092C + 0.004C^2 - 10^{-0.58C}$	0.650 for $C \leq 5$ 0.300 for $C > 5$	In compounds containing $>\text{CO}/\text{—O—}$ groups special value for the combination $\Delta N = 0.125$ (diacetonealcohol)	
Unsaturated primary	$0.615 - 0.092C + 0.004C^2 - 10^{-0.58C}$	0.175		
Unsaturated tertiary	$0.615 - 0.092C + 0.004C^2 - 10^{-0.58C}$	0.425		

Structure	$\Delta\eta_B$	ΔN	Remarks	
In cyclic alcohols	0.270	0.150	(i) In compounds containing $-\text{NH}_2$ or $-\text{CHO}$ groups in ortho position, special value for the combination, $\Delta N = 0.075$ (2-nitrophenol, salicylaldehyde)	
Phenolic	0.270	0.200		
			(ii) In compounds containing $-\text{O}-$ $\Delta N_{\text{cor}} = 0.050$ (4-methoxyphenol)	
Contribution of nitrogen groups				
Group	Structure	$\Delta\eta_B^a$	ΔN	Remarks
$-\text{NH}_2$	In aliphatic <i>n</i> -amines	0.170	0.100	(i) $\Delta\eta_{B,\text{cor}} = 0.100$ in $\text{NH}_2 - (\text{CH}_2)_n - \text{NH}_2$ (ethylenediamine)
				(ii) in compounds containing $>\text{COO}$ $\Delta\eta_{B,\text{cor}} = 0.080$ (acetamide)
$-\text{NH}_2$	Aliphatic isoamines attached to $>\text{CH}$	0.200	0.100	(iii) In compounds containing $-\text{COO}$, $\Delta N_{\text{cor}} = 0.100$ (ethyl carbamate) (isopropylamine)
$-\text{NH}_2$	In monocyclic compounds, attached to side chain	0.170	0.100	(benzylamine)
$-\text{NH}_2$	In monocyclic compounds, attached to ring carbon	0.205	0.150	(i) For compounds containing $-\text{O}-$ $\Delta N_{\text{cor}} = -0.050$ (2-methoxyaniline)
				(ii) In cyclic compounds containing $-\text{COO}-$ group, special value for the combination, $\Delta N = 0.100$ (ethylanthranilate)
$-\text{NH}_2$	In other aromatics	0.150	0.100	(1-naphthylamine)
$>\text{NH}$	In aliphatics	0.020	0.075	In compounds containing $-\text{OH}$ special value for the combination, $\Delta N = 0.300$ (aminoethyl ethanolamine)
$>\text{NH}$	In aromatic compounds, attached to side chain	0.020	0.075	(dibenzylamine)
$>\text{NH}$	In aromatic compounds, attached to ring carbon	0.020	0.100	
NH	Ring	0.160	0.100	

TABLE 9-10 Sastri and Rao (1992) Group Contributions for η_B and N in Eq. (9-11.2) (*Continued*)

Contribution of nitrogen groups (continued)				
Group	Structure	$\Delta\eta_B^a$	ΔN	Remarks
$>N-$	In aliphatics	-0.115	0.050	For aliphatic compounds containing $>CO$ $\Delta\eta_{Bcor} = 0.080$ (dimethyl acetamide)
$>N-$	In aromatic compounds, attached to side chain	-0.115	0.050	(tribenzylamine)
$>N-$	In aromatic compounds, attached to ring carbon	-0.060	0.050	
$>N-$	Ring	0.100	0.050	In compounds containing $-CN$ or halogen, $\Delta N_{cor} = -0.050$
$-NO_2$	In aliphatics	0.180	0.050	For multiple occurrences $\Delta N_{cor} = 0.050$
	In aromatics	0.160	0.050	(i) for multiple occurrences $\Delta N_{cor} = 0.050$ and $\Delta\eta_{Bcor} = 0.070$ (<i>m</i> -dinitrobenzene) (ii) In compounds containing $-OH$ (phenolic) in ortho position, special value for the combination, $\Delta N_{cor} = 0.075$ (2-nitrophenol)
$-CN$		0.135	0.025	(i) For multiple occurrence, $\Delta N_{cor} = 0.075$ (ii) With N in ring, $\Delta N_{cor} = -0.050$
Contribution of sulphur groups				
Functional group/structure	$\Delta\eta_B$	ΔN		
$-S-$ Non-ring	0.045	0.000		
$-S-$ ring	0.150	0.050		
$-SH$	0.150	0.025		

^a $\Delta\eta_B = 0.080$ for $-H$ in compounds containing hydrocarbon functional groups (e.g. formamide)

TABLE 9-11 Comparison of Calculated and Experimental Viscosities of Liquids

Compound	<i>T</i> , K	η (exp.) cP**	Percent error* in liquid viscosity calculated by the method of		
			Orrick and Erbar	Sastri and Rao	Przedzdiecki and Sridhar
Acetone	183	2.075	-25	-3.5	-11
	213	0.982	-6.7	1.9	-4.6
	273	0.389	-8.3	3.6	-2.3
	303	0.292	-9.4	1.6	-1.2
	333	0.226	-8.3	1.9	0.2
Acetic acid	283	1.450	-22	-15	8.6
	313	0.901	-15	-15	0
	353	0.561	-9.5	-17	-1.3
	383	0.416	-5.3	-16	0.3
Aniline	263	13.4	—	-24	—
	293	4.38	—	-4.8	—
	333	1.520	—	8.1	-49
	393	0.658	—	-9.6	-33
Benzene	278	0.826	-45	-8.5	1.1
	313	0.492	-35	-6.6	7.3
	353	0.318	-26	-5.5	12
	393	0.219	-46	-5.7	18
	433	0.156	-7.1	-6.4	23
	463	0.121	5.1	-9.5	28
<i>n</i> -Butane	183	0.630	-14	1.6	-9
	213	0.403	-20	-2.8	-8.9
	273	0.210	-23	-0.4	-5.8
1-Butene	163	0.79	-22	0.9	-13
	193	0.45	-20	-2.9	-9.6
	233	0.26	-18	-2.5	-3.3
<i>n</i> -Butyl alcohol	273	5.14	-2.1	0.3	—
	313	1.77	-1.6	-3.4	—
	353	0.762	0.5	-2	—
	393	0.394	-1.4	1.4	—
Carbon tetrachloride	273	1.369	20	-4.4	-24
	303	0.856	22	-2	-15
	343	0.534	20	-0.1	-6.7
	373	0.404	19	-0.7	-2.8
Chlorobenzene	273	1.054	1.4	2.7	-8.3
	313	0.639	-0.6	0.8	-7
	353	0.441	-0.9	-1.2	-5.2
	393	0.326	-5.1	-0.9	-3.8
Chloroform	273	0.700	40	7.4	-11
	303	0.502	34	5.7	-8.1
	333	0.390	27	3.6	-7.9
Cyclohexane	278	1.300	-51	-29.7	-38
	333	0.528	-38	-16.4	-22
Cyclopentane	293	0.439	-32	-5.1	-33
	323	0.323	-28	-7.8	-29

TABLE 9-11 Comparison of Calculated and Experimental Viscosities of Liquids
(Continued)

Compound	T, K	η (exp.) cP**	Percent error* in liquid viscosity calculated by the method of		
			Orrick and Erbar	Sastri and Rao	Przeddziecki and Sridhar
2,2-Dimethylpropane	258	0.431	-3.5	-24.3	20
	283	0.281	-0.8	-15.1	30
Ethane	98	0.985	30	53.6	-24
	153	0.257	-12	26.4	-14
	188	0.162	-22	21.3	-13
Ethylene chloride	273	1.123	-43	-20.7	—
	313	0.644	-35	-15.3	—
	353	0.417	-27	-8.8	—
Ethyl alcohol	273	1.770	27	-14.1	—
	313	0.826	3.5	-6	—
	348	0.465	-5.4	7.7	—
Ethyl acetate	293	0.458	-4.2	-5.5	-16
	353	0.246	0.4	-1.2	-5.3
	413	0.153	7.4	-9.7	-1.8
	463	0.0998	27	-2.2	4.8
Ethylbenzene	253	1.240	-2.9	19.7	-33
	313	0.535	-1.2	7.3	-23
	373	0.308	-1.7	0.1	-16
	413	0.231	-1.2	-1.9	-13
Ethyl bromide	293	0.395	27	0	-23
	333	0.269	32	2.2	-17
	373	0.199	36	4.6	-16
Ethylene	103	0.70	-25	-0.7	25
	133	0.31	-27	-2.3	-17
	173	0.15	-22	4.8	-6.4
Ethyl ether	273	0.289	0	2.7	0
	293	0.236	0	1.6	2.2
	333	0.167	2	-3.5	4
	373	0.118	1	5.5	7.4
Ethyl formate	273	0.507	-18	6.8	-16
	303	0.362	-17	6.6	-11
	328	0.288	-16	7	-9.6
<i>n</i> -Heptane	183	3.77	-21	-33.2	-1.7
	233	0.965	-0.5	-11.3	-27
	293	0.418	-1.9	-7.2	-21
	373	0.209	-3.3	-1	-17
<i>n</i> -Hexacontane (C ₆₀ H ₁₂₂)	408	7.305	18	37	—
	466	3.379	-63	19	—
<i>n</i> -Hexane	213	0.888	2.9	-2.3	-8.3
	273	0.381	-2.4	-2.4	-8.2
	343	0.205	-4.9	1.2	-7.1

TABLE 9-11 Comparison of Calculated and Experimental Viscosities of Liquids
(Continued)

Compound	T, K	η (exp.) cP**	Percent error* in liquid viscosity calculated by the method of		
			Orrick and Erbar	Sastri and Rao	Przedzdiecki and Sridhar
Isobutane	193	0.628	-23	1.1	-37
	233	0.343	-25	-12.2	-29
	263	0.239	-24	-17.1	-23
Isopropyl alcohol	283	3.319	-24	-16.2	—
	303	1.811	-15	9.8	—
	323	1.062	-10	4.5	—
Methane	88	0.226	60	1.5	-11
	113	0.115	23	-20.1	-4.3
2-Methylbutane	223	0.550	-13	-10.8	-30
	253	0.353	-12	0.3	-21
	303	0.205	-10	-1.9	-12
<i>n</i> -Pentane	153	2.35	-1	-1.7	11
	193	0.791	3.8	0.1	-7
	233	0.428	-3.3	7.3	-6
	273	0.279	-8.2	2.9	-4.7
	303	0.216	-11	0.6	-4.9
Phenol	323	3.020	0	1.5	-50
	373	0.783	37	12.5	-5.4
Propane	133	0.984	-1.5	45.4	-23
	193	0.327	-22	14	-19
	233	0.205	-25	-1.7	-16
<i>n</i> -Propyl alcohol	283	2.897	-9.1	0.8	—
	313	1.400	-9.8	-6.1	—
	373	0.443	-6.5	-7.4	—
Toluene	253	1.070	-19	0.4	-33
	293	0.587	-13	0.7	-24
	333	0.380	-10	-2.1	-16
	383	0.249	-6.8	-5.1	-10
<i>o</i> -Xylene	273	1.108	3.1	-5.1	-5.5
	313	0.625	5	-4.5	-4.8
	373	0.345	3.7	4.5	-0.3
	413	0.254	3.6	1.8	1.9
<i>m</i> -Xylene				-2.7	
	273	0.808	1.1	-2.6	1.9
	313	0.492	1.4	-0.4	1.8
	353	0.340	0.3	2	2.9
	413	0.218	1.4	3.4	4.6

*[(calc - exp)/exp] \times 100.

**Data from Aasen, et al. (1990), Amdur and Mason (1958), and Landolt-Bornstein (1955).

solution o-xylene has 4=CH— (ring, not alicyclic), 2=C< (ring, not alicyclic) and 2 —CH₃ groups. There is a correction to η_{Bcor} of 0.07 for multiple substitution. With values from Table 9-10:

$$\eta_B = 4 \times 0.05 - 2 \times 0.12 + 2 \times 0.105 + 0.07 = 0.24 \text{ mPa}\cdot\text{s}$$

$$N = 0.2 + 0.05 = 0.25$$

ethanol has one —CH₃, one >CH₂ (non-ring) and one —OH. With values from Table 9-10:

$$\eta_B = 0.105 + 0.615 - 0.092 \times 2 + 0.004 \times 4 - 10^{-0.58 \times 2} = 0.483 \text{ mPa}\cdot\text{s}$$

$$N = 0.2 + 0.15 = 0.35$$

ethylbenzene has 5 =CH— (ring, not alicyclic), one =C< (ring not alicyclic), one —CH₃, and one —CH₂— (non-ring). There is a branching correction to ΔN of 0.025. With values from Table 9-10:

$$\eta_B = 5 \times 0.05 - 0.12 + 0.105 = 0.235 \text{ mPa}\cdot\text{s}$$

$$N = 0.2 + 0.025 = 0.225$$

2-3 dimethylbutane has 4 —CH₃ and 2 >CH— (non-ring). The value of ΔN of 0.05 is applied only once. With values from Table 9-10:

$$\eta_B = 4 \times 0.105 - 2 \times 0.11 = 0.2 \text{ mPa}\cdot\text{s}$$

$$N = 0.2 + 0.05 = 0.25$$

o-chlorophenol has 4=CH— (ring, not alicyclic), 2=C< (ring, not alicyclic), one —Cl attached to an “other”, and one —OH (phenolic). Note that the —Cl contribution to ΔN of 0.025 is not used. Footnote b in the halogen section of Table 9-10 applies because of the presence of the non-hydrocarbon —OH group. With values from Table 9-10:

$$\eta_B = 4 \times 0.05 - 2 \times 0.12 + 0.17 + 0.27 = 0.4 \text{ mPa}\cdot\text{s}$$

$$N = 0.2 + 0.2 - 0.075 = 0.325$$

Przedziecki and Sridhar (1985) Method

In this technique, the authors propose using the Hildebrand-modified Batschinski equation (Batschinski, 1913; Hildebrand, 1971; Vogel and Weiss, 1981)

$$\eta_L = \frac{V_o}{E(V - V_o)} \quad (9-11.6)$$

where η_L = liquid viscosity, cP

V = liquid molar volume, cm³/mol

and the parameters E and V_o are defined below.

$$E = -1.12 + \frac{V_c}{12.94 + 0.10 M - 0.23 P_c + 0.0424 T_{fp} - 11.58(T_{fp}/T_c)} \quad (9-11.7)$$

$$V_o = 0.0085\omega T_c - 2.02 + \frac{V_m}{0.342(T_{fp}/T_c) + 0.894} \quad (9-11.8)$$

where T_c = critical temperature, K

P_c = critical pressure, bar

V_c = critical volume, cm³ /mol

M = molecular weight, g/mol

T_{fp} = freezing point, K

ω = acentric factor

V_m = liquid molar volume at T_{fp} , cm³/mol

Thus, to use Eq. (9-11.6), one must have values for T_c , P_c , V_c , T_{fp} , ω , and V_m in addition to the liquid molar volume V at the temperature of interest. The authors recommend that V_m and V be estimated from T_{fp} and T by the Gunn-Yamada (1971) method. In the Gunn-Yamada method, one accurate value of V is required in the temperature range of applicability of Eq. (9-11.6). We define this datum point as V^R at T^R ; then at any other temperature T ,

$$V(T) = \frac{f(T)}{f(T^R)} V^R \quad (9-11.9)$$

where

$$f(T) = H_1(1 - \omega H_2) \quad (9-11.10)$$

$$H_1 = 0.33593 - 0.33953T_r + 1.51941T_r^2 - 2.02512T_r^3 + 1.11422T_r^4 \quad (9-11.11)$$

$$H_2 = 0.29607 - 0.09045T_r - 0.04842T_r^2 \quad (9-11.12)$$

Equation (9-11.6) was employed with Eqs. (9-11.7) to (9-11.12) to estimate liquid viscosities for the compounds in Table 9-11. The values of T_c , P_c , V_c , T_{fp} , and ω , were obtained from Appendix A. The reference volume for each compound was calculated from the liquid density datum value given in Appendix A. Large errors were noted for alcohols, and those results are not included in the table. For other compounds, the errors varied widely and, except for a few materials, the technique underestimated the liquid viscosity. Larger errors were normally noted at low temperatures, but that might have been expected from the form of Eq. (9-11.6). That is, because V_o is of the order of the volume at the freezing point and $\eta_L \propto (V - V_o)^{-1}$, the estimated value of η_L becomes exceedingly sensitive to the choice of V . This problem was emphasized by Luckas and Lucas (1986), who suggest that Eq. (9-11.6) should not be used below T_r values of about 0.55.

Example 9-19 Use the Przedzicki and Sridhar correlation to estimate the liquid viscosity of toluene at 383 K. The experimental value is 0.249 cP (Vargaftik, et al., 1996).

solution From Appendix A, for toluene (slightly different values were used to calculate the results shown in Table 9-11)

$$\begin{aligned}T_c &= 591.75 \text{ K} \\P_c &= 41.08 \text{ bar} \\V_c &= 316 \text{ cm}^3/\text{mol} \\T_{fp} &= 178 \text{ K} \\M &= 92.14 \text{ g/mol} \\\omega &= 0.264 \\V_L &= 106.87 \text{ cm}^3/\text{mol at } 298.15 \text{ K}\end{aligned}$$

With $T^R = 298.15 \text{ K}$, and with Eqs. (9-11.9) to (9-11.12),

$$T_r^R = \frac{298.15}{591.75} = 0.504$$

$$\begin{aligned}H_1(T_r^R) &= 0.33593 - (0.33953)(0.504) + (1.51941)(0.504)^2 - (2.02512)(0.504)^3 \\&\quad + (1.11422)(0.504)^4 = 0.363\end{aligned}$$

$$H_2(T_r^R) = 0.29607 - (0.09045)(0.504) - (0.04842)(0.504)^2 = 0.238$$

$$f(T^R) = 0.363[1 - (0.264)(0.238)] = 0.340$$

Similarly,

	$T, \text{ K}$	T_r	H_1	H_2	$f(T)$
T_{fp}	178	0.301	0.325	0.264	0.303
T^R	383	0.647	0.399	0.217	0.376

Then
$$V_m = \frac{0.303}{0.340}(106.87) = 95.2 \text{ cm}^3/\text{mol}$$

$$V = \frac{0.376}{0.340}(106.87) = 118.2 \text{ cm}^3/\text{mol}$$

This value for V agrees with that given in Vargaftik, et al. (1996). With Eqs. (9-11.7) and (9-11.8)

$$\begin{aligned}E &= -1.12 + 316/[12.94 + (0.10)(92.14) - (0.23)(41.08) + (0.0424)(178) \\&\quad - (11.58)(178/591.8)] = 17.72\end{aligned}$$

$$\begin{aligned}V_o &= (0.0085)(0.264)(591.75) - 2.02 + \frac{95.2}{[(0.342)(178/591.8) + 0.894]} \\&= 94.8 \text{ cm}^3/\text{mol}\end{aligned}$$

Then, with Eq. (9-11.6)

$$\eta_L = \frac{94.8}{17.72(118.2 - 94.8)} = 0.229 \text{ cP}$$

$$\text{Error} = \frac{0.229 - 0.249}{0.249} \times 100 = -8\%$$

Other Correlations

Other viscosity-correlating methods have been proposed, and a number of these are summarized in Mehrotra, et al. (1996) and Monnery, et al. (1995). Other recent correlations are given in Mehrotra (1991), and the earlier literature was reviewed in the 4th Edition of this book.

Recommendations for Estimating Low-temperature Liquid Viscosities

Three estimation methods have been discussed. In Table 9-11, calculated liquid viscosities are compared with experimental values for 36 different liquids (usually of simple structure). Large errors may result, as illustrated for all methods. The method of Przedzicki and Sridhar should not be used for alcohols.

The method of Sastri and Rao assumes that the temperature dependence of η_L is related to the temperature dependence of the vapor pressure, whereas the Orrick and Erbar method is slightly modified to include the liquid density. Neither is reliable for highly branched structures or for inorganic liquids and the Orrick-Erbar method cannot be used for sulfur compounds. Both are limited to a temperature range from somewhat above the freezing point to about $T_r \approx 0.75$. Przedzicki and Sridhar's method employs the Hildebrand equation, which necessitates knowledge of liquid volumes.

It is recommended that, in general, the method of Sastri and Rao be used to estimate low-temperature liquid viscosities. Errors vary widely, but should be less than 10 to 15% in most instances.

9-12 ESTIMATION OF LIQUID VISCOSITY AT HIGH TEMPERATURES

Low-temperature viscosity correlations as covered in Sec. 9-10 usually assume that $\ln \eta_L$ is a linear function of reciprocal absolute temperature. Above a reduced temperature of about 0.7, this relation is no longer valid, as illustrated in Fig. 9-10. In the region from about $T_r = 0.7$ to near the critical point, many estimation methods are of a corresponding states type that resemble or are identical with those used in the first sections of this chapter to treat gases. For this temperature range, Sastri (1998) recommends

$$\ln \eta = \left[\frac{\ln \eta_B}{\ln(\alpha \eta_B)} \right]^\phi \ln(\alpha \eta_B) \quad (9-12.1)$$

where η is in $\text{mPa} \cdot \text{s}$

η_B = viscosity at T_b in mPa · s, from contributions in Table 9-10

$\alpha = 0.1175$ for alcohols and 0.248 for other compounds

$$\phi = \frac{1 - T_r}{1 - T_{br}} \quad (9-12.2)$$

where $T_r = T/T_c$
 $T_{br} = T_b/T_c$

Sastri reports average deviations of 10% for $T_r > 0.9$ and 6% for $T_{br} < T_r < 0.9$.

Example 9-20 Estimate the saturated liquid viscosity of *n*-propanol at 433.2 K by using Eq. (9-12.1). The experimental value is 0.188 cP.

solution From Appendix A, $T_b = 370.93$ K and $T_c = 536.78$ K. With contributions from Table 9-10, $\eta_B = 0.105 + 0.615 - 0.092 \times 3 + 0.004 \times 9 - 10^{-3 \times 0.58} = 0.462$ mPa · s = 462 μ Pa · s. From Eq. (9-12.2)

$$\phi = \frac{1 - 433.2/536.78}{1 - 370.93/536.78} = 0.624$$

With $\alpha = 0.1175$, Eq. (9-12.1) gives

$$\ln \eta = \ln(0.1175 \times 462) \left[\frac{\ln(462)}{\ln(0.1175 \times 462)} \right]^{0.624}$$

$$\eta = 185 \mu\text{Pa} \cdot \text{s} = 0.185 \text{ cP}$$

$$\text{Error} = \frac{0.185 - 0.188}{0.188} \times 100 = -1.6\%$$

A more general estimation method would logically involve the extension of the high-pressure gas viscosity correlations described in Sec. 9-6 into the liquid region. Two techniques have, in fact, been rather widely tested and found reasonably accurate for reduced temperatures above about 0.5. These methods are those of Chung, et al. (1988) and Brulé and Starling (1984). Both methods use Eq. (9-6.16), but they have slightly different coefficients to compute some of the parameters. The Chung, et al. form is preferable for simple molecules and will treat polar as well as nonpolar compounds. The Brulé and Starling relation was developed primarily for complex hydrocarbons, and the authors report their predictions are within 10% of experimental values in the majority of cases. The Chung, et al. method has a similar accuracy for most nonpolar compounds, but significantly higher errors can occur with polar, halogenated, or high-molecular weight compounds. In both cases, one needs accurate liquid density data, and the reliability of the methods decreases significantly for T_r less than about 0.5. The liquids need not be saturated; subcooled compressed liquid states simply reflect a higher liquid density. The Chung, et al. technique was illustrated for dense gas ammonia in Example 9-12. The procedure is identical when applied to high-temperature liquids.

Discussion

The quantity of accurate liquid viscosity data at temperatures much above the normal boiling point is not large. In addition, to test estimation methods such as those of Chung, et al. or Brulé and Starling, one needs accurate liquid density data under

the same conditions which apply to the viscosity data. This matching makes it somewhat difficult to test the methods with many compounds. However, Brulé and Starling developed their technique so that they would be coupled to a separate computation program using a modified BWR equation of state to provide densities. They report relatively low errors, and this fact appears to confirm the general approach (See also Brulé and Starling, 1984). Hwang, et al. (1982) have proposed viscosity (as well as density and surface tension) correlations for coal liquids.

Regardless of what high-temperature estimation method is chosen, there is the problem of joining both high- and low-temperature estimated viscosities should that be necessary.

9-13 LIQUID MIXTURE VISCOSITY

Essentially all correlations for liquid mixture viscosity refer to solutions of liquids below or only slightly above their normal boiling points; i.e., they are restricted to reduced temperatures (of the pure components) below about 0.7. The bulk of the discussion below is limited to that temperature range. At the end of the section, however, we suggest approximate methods to treat high-pressure, high-temperature liquid mixture viscosity.

At temperatures below $T_r \approx 0.7$, liquid viscosities are very sensitive to the structure of the constituent molecules (See Sec. 9-11). This generality is also true for liquid mixtures, and even mild association effects between components can often significantly affect the viscosity. For a mixture of liquids, the shape of the curve of viscosity as a function of composition can be nearly linear for so-called ideal mixtures. But systems that contain alcohols and/or water often exhibit a maximum or a minimum and sometimes both (Irving, 1977a).

Almost all methods to estimate or correlate liquid mixture viscosities assume that values of the viscosities of the pure components are available. Thus the methods are interpolative. Nevertheless, there is no agreement on the best way to carry out the interpolation. Irving (1977) surveyed more than 50 equations for binary liquid viscosities and classified them by type. He points out that only very few do not have some adjustable constant that must be determined from experimental mixture data and the few that do not require such a parameter are applicable only to systems of similar components with comparable viscosities. In a companion report from the National Engineering Laboratory, Irving (1977a) has also evaluated 25 of the more promising equations with experimental data from the literature. He recommends the one-constant Grunberg-Nissan (1949) equation [see Eq. (9-13.1)] as being widely applicable yet reasonably accurate except for aqueous solutions. This NEL report is also an excellent source of viscosity data tabulated from the literature. Other data and literature sources for data may be found in Aasen et al. (1990), Aucejo, et al. (1995), supplementary material of Cao, et al. (1993), Franjo, et al. (1995), Kouris and Panayiotou (1989), Krishnan, et al. (1995, 1995a), Kumagai and Takahashi (1995), Petrino, et al. (1995), Stephan and Hildwein (1987), Stephan and Heckenberger (1988), Teja, et al., (1985), and Wu, et al. (1998).

Method of Grunberg and Nissan (1949)

In this procedure, the low-temperature liquid viscosity for mixtures is given as

$$\ln \eta_m = \sum_i x_i \ln \eta_i + \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n x_i x_j G_{ij} \quad (9-13.1)$$

or, for a binary of 1 and 2,

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \quad (9-13.2)$$

since $G_{ii} = 0$. In Eqs. (9-13.1) and (9-13.2), x is the liquid mole fraction and G_{ij} is an interaction parameter which is a function of the components i and j as well as the temperature (and, in some cases, the composition). This relation has probably been more extensively examined than any other liquid mixture viscosity correlation. Isdale (1979) presents the results of a very detailed testing using more than 2000 experimental mixture datum points. When the interaction parameter was regressed from experimental data, nonassociated mixtures and many mixtures containing alcohols, carboxylic acids, and ketones were fitted satisfactorily. The overall root mean square deviation for the mixtures tested was 1.6%. More recently, Isdale, et al. (1985) proposed a group contribution method to estimate the binary interaction parameter G_{ij} at 298 K.

The procedure to be followed is:

1. For a binary of i and j , select i by following the priority rules below. (j then becomes the second component.)

- a. i = an alcohol, if present
- b. i = an acid, if present
- c. i = the component with the most carbon atoms
- d. i = the component with the most hydrogen atoms
- e. i = the component with the most $-\text{CH}_3$ groups

$G_{ij} = 0$ if none of these rules establish a priority.

2. Once the decision has been made which component is i and which is j , calculate $\Sigma\Delta_i$ and $\Sigma\Delta_j$ from the group contributions in Table 9-12.

3. Determine the parameter W . (If either i or j contains atoms other than carbon and hydrogen, set $W = 0$ and go to step 4.) Let the number of carbon atoms in i be N_i and that in j be N_j .

$$W = \frac{(0.3161)(N_i - N_j)^2}{N_i + N_j} - (0.1188)(N_i - N_j) \quad (9-13.3)$$

4. Calculate G_{ij} from

$$G_{ij} = \Sigma\Delta_i - \Sigma\Delta_j + W \quad (9-13.4)$$

G_{ij} is sometimes a function of temperature. However, existing data suggest that, for alkane-alkane solutions or for mixtures of an associated component with an unassociated one, G_{ij} is independent of temperature. However, for mixtures of non-associated compounds (but not of only alkanes) or for mixtures of associating compounds, G_{ij} is a mild function of temperature. Isdale, et al. (1985) suggest for these latter two cases,

$$G_{ij}(T) = 1 - [1 - G_{ij}(298)] \frac{573 - T}{275} \quad (9-13.5)$$

where T is in kelvins.

Example 9-21 Estimate the viscosity of a mixture of acetic acid and acetone at 323 K (50°C) that contains 70 mole percent acetic acid. Isdale, et al. quote the experimental value to be 0.587 cP, and, at 50°C, the viscosities of pure acetic acid and acetone are 0.798 and 0.241 cP, respectively.

TABLE 9-12 Group Contributions for G_{ij} at 298 K

Group	Notes	Value of Δ_i
—CH ₃		−0.100
>CH ₂		0.096
>CH—		0.204
>C<		0.433
Benzene ring		0.766
Substitutions:		
Ortho		0.174
Meta		—
Para		0.154
Cyclohexane ring		0.887
—OH	Methanol	0.887
	Ethanol	−0.023
	Higher aliphatic alcohols	−0.443
>C=O	Ketones	1.046
—Cl		0.653−0.161 N_{Cl}
—Br		−0.116
—COOH	Acid with:	
	Nonassociated liquids	−0.411 + 0.06074 N_C
	Ketones	1.130
	Formic acid with ketones	0.167

N_{Cl} = number of chlorine atoms in the molecule.

N_C = total number of carbon atoms in both compounds.

solution First we must estimate G_{ij} at 298 K. Component i is acetic acid (priority rule b). Since the mixture contains atoms other than carbon and hydrogen (i.e., oxygen), $W = 0$. Then, with Table 9-12,

$$\Sigma\Delta_i \text{ (acetic acid)} = \text{—CH}_3 + \text{—COOH} = -0.100 + 1.130 = 1.030$$

$$\Sigma\Delta_j \text{ (acetone)} = (2)(\text{—CH}_3) + \text{>C=O} = (2)(-0.100) + 1.046 = 0.846$$

With Eq. (9-13.4),

$$G_{ij} = 1.030 - 0.846 = 0.184 \text{ at } 298 \text{ K}$$

At 50°C = 323 K, we need to adjust G_{ij} with Eq. (9-13.5).

$$G_{ij}(323 \text{ K}) = 1 - \frac{(1 - 0.184)(573 - 323)}{275} = 0.258$$

Then, using Eq. (9-13.2),

$$\ln \eta_m = (0.7) \ln (0.798) + (0.3) \ln (0.241) + (0.7)(0.3)(0.258) = -0.531$$

$$\eta_m = 0.588 \text{ cP}$$

This estimated value is essentially identical with the experimental result of 0.587 cP.

To summarize the Isdale modification of the Grunberg-Nissan equation, for each possible binary pair in the mixture, first decide which component is to be labeled i and which j by the use of the priority rules. Determine $\Sigma\Delta_i$ and $\Sigma\Delta_j$ by using

Table 9-12 and W from Eq. (9-13.3), if necessary. Use Eq. (9-13.4) to calculate G_{ij} . Correct for temperatures other than 298 K, if necessary, with Eq. (9-13.5). With the values of G_{ij} so determined, use either Eq. (9-13.1) or (9-13.2) to determine the viscosity of the liquid mixture. This technique yields quite acceptable estimates of low-temperature liquid mixture viscosities for many systems, but Table 9-12 does not allow one to treat many types of compounds. Also, the method does not cover aqueous mixtures.

UNIFAC-VISCO Method (Chevalier, et al., 1988; Gaston-Bonhomme, et al., 1994)

Gaston-Bonhomme, Petrino and Chevalier have modified the UNIFAC activity coefficient method (described in Chap. 8) to predict viscosities. In this method, viscosity is calculated by

$$\ln \eta_m = \sum_i x_i \ln(\eta_i V_i) - \ln V_m + \frac{\Delta^* g^{EC}}{RT} + \frac{\Delta^* g^{ER}}{RT} \quad (9-13.6)$$

The combinatorial term is the same as in the UNIQUAC model (see Table 8-8) and is calculated by

$$\frac{\Delta^* g^{EC}}{RT} = \sum_i x_i \ln \frac{\phi_i}{x_i} + \frac{z}{2} \sum_i q_i x_i \ln \frac{\theta_i}{\phi_i} \quad (9-13.7)$$

where z is the coordination number, equal to 10, θ_i and ϕ_i are the molecular surface area fraction and molecular volume fraction, respectively, given by

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (9-13.8)$$

and

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad (9-13.9)$$

where q_i , the van der Waals' surface area, and r_i , the van der Waals' volume of component i , are found by summation of the corresponding group contributions. Thus, if $n_k^{(i)}$ is the number of groups of type k in the molecule i ,

$$q_i = \sum_k n_k^{(i)} Q_k \quad (9-13.10)$$

$$r_i = \sum_k n_k^{(i)} R_k \quad (9-13.11)$$

where Q_k and R_k are the constants representing the group surface and size and are given in Table 9-13. These values match the UNIFAC values in Table 8-23 in cases where groups are defined the same. The residual term in Eq. (9-13.6) is calculated by

TABLE 9-13 UNIFAC-VISCO, Group Volume and Surface Area Parameters

Group k	R_k	Q_k
$\text{CH}_2, \text{CH}_{2\text{cy}}$	0.6744	0.540
CH_3	0.9011	0.848
CH_{ar}	0.5313	0.400
Cl	0.7910	0.724
CO	0.7713	0.640
COO	1.0020	0.880
OH	1.0000	1.200
CH_3OH	1.4311	1.432

$$\frac{\Delta^*g^{ER}}{RT} = - \sum x_i \ln \gamma_i^{*R} \quad (9-13.12)$$

where

$$\ln \gamma_i^{*R} = \sum_k n_k^{(i)} [\ln \gamma_k^* - \ln \gamma_k^{*(i)}] \quad (9-13.13)$$

and

$$\ln \gamma_k^* = Q_k \left[(1 - \ln \left(\sum_m \Theta_m \Psi_{mk}^* \right)) - \sum_m \frac{\Theta_m \Psi_{km}^*}{\sum_n \Theta_n \Psi_{nm}^*} \right] \quad (9-13.14)$$

$$\Theta_m = \frac{Q_m X_m}{\sum_k X_k Q_k} \quad (9-13.15)$$

In Eq. (9-13.15), Θ_m is the surface area fraction in the mixture of groups and X_m is the mole fraction in the mixture of groups. Except for the minus sign in Eq. (9-13.12), these last four equations are identical to those in the UNIFAC method described in Chap 8. However, the groups are chosen differently and the interaction parameters are different and are calculated by

$$\Psi_{nm}^* = \exp \left(- \frac{\alpha_{nm}}{298} \right) \quad (9-13.16)$$

Values of α_{nm} are given in Table 9-14. γ_k^* is the activity coefficient of group k in a mixture of groups in the actual mixture, and $\gamma_k^{*(i)}$ is the activity coefficient of group k in a mixture of groups formed from the groups in pure component i . Groups in branched hydrocarbons and substituted cyclic and aromatic hydrocarbons are chosen as follows

TABLE 9-14 UNIFAC-VISCO Group Interaction Parameters, α_{nm}

n/m	CH ₂	CH ₃	CH _{2cy}	CH _{ar}	Cl	CO	COO	OH	CH ₃ OH
CH ₂	0	66.53	224.9	406.7	60.30	859.5	1172.0	498.6	-219.7
CH ₃	-709.5	0	-130.7	-119.5	82.41	11.86	-172.4	594.4	-228.7
CH _{2cy}	-538.1	187.3	0	8.958	215.4	-125.4	-165.7	694.4	-381.53
CH _{ar}	-623.7	237.2	50.89	0	177.2	128.4	-49.85	419.3	-88.81
Cl	-710.3	375.3	-163.3	-139.8	0	-404.3	-525.4	960.2	-165.4
CO	586.2	-21.56	740.6	-117.9	-4.145	0	29.20	221.5	55.52
COO	541.6	-44.25	416.2	-36.17	240.5	22.92	0	186.8	69.62
OH	-634.5	1209.0	-138	197.7	195.7	664.1	68.35	0	416.4
CH ₃ OH	-526.1	653.1	751.3	51.31	-140.9	-22.59	-286.2	-23.91	0

Type of compound	Actual group	Representation
branched cyclic	$>\text{CH}-\text{CH}_3$	2 CH_2 groups
	$>\text{CH}_{\text{cy}}-\text{CH}_3$	1 $\text{CH}_{2\text{cy}}$ + 1 CH_2
	$>\text{C}_{\text{cy}}-(\text{CH}_3)_2$	1 CH_{acy} + 2 CH_2
aromatic	$>\text{C}_{\text{ar}}-\text{CH}_3$	1 CH_{ar} + 1 CH_2

Table 9-15 compares results calculated with the UNIFAC-VISCO method to experimental values. Of all the methods evaluated, the UNIFAC-VISCO method was the only one that demonstrated any success in predicting viscosities of mixtures of compounds with large size differences. The method has also been successfully applied to ternary and quaternary alkane systems. The average absolute deviation for 13 ternary alkane systems was 2.6%, while for four quaternary systems it was 3.6%. The method is illustrated in Example 9-22.

Example 9-22 Use the UNIFAC-VISCO method to estimate the viscosity of a mixture of 35.4 mole% *n*-decane (1) and 64.6 mole% *n*-tetratetracontane, $\text{C}_{44}\text{H}_{90}$ (2) at 397.49 K. The experimental viscosity and density (Aasen, et al., 1990) are 3.278 cP and 0.7447 g/cm³.

solution From Aasen, et al. (1990), $\eta_1 = 0.2938$ cP, $\eta_2 = 4.937$ cP, $V_1 = 220$ g/cm³, and $V_2 = 815.5$ g/cm³.

$$V_m = \frac{\sum_i x_i M_i}{\rho_m} = \frac{0.354 \times 142.28 + 0.646 \times 619.16}{0.7447} = 604.7 \text{ cm}^3/\text{mol}$$

In decane, there are 8 CH_2 groups and 2 CH_3 groups. In tetratetracontane, there are 42 CH_2 groups and 2 CH_3 groups. Equations (9-13.10) and (9-13.11) give

TABLE 9-15 Comparison of Calculated and Experimental Liquid Mixture Viscosities

1 st component	2 nd component	x_1	T , K	η_{exp} mPa·s	Ref*	η_{calc} mPa·s	% deviation
<i>n</i> -C ₁₀ H ₂₂	<i>n</i> -C ₆₀ H ₁₂₂	0.749	384.1	3.075	1	2.309	-25
		0.749	446.4	1.423	1	1.275	-10
	<i>n</i> -C ₄₄ H ₉₀	0.354	368.8	5.286	1	5.256	-0.6
		0.354	464.1	1.465	1	1.654	13
butane	squalane	0.695	374.1	2.318	1	1.960	-15
		0.839	293.1	1.060	2	0.8812	-17
		0.5113	298.1	0.681	3	0.6403	-6.0
ethanol	benzene	0.3321	298.1	0.4599	4	0.4553	-1.0
acetone	benzene	0.3321	298.1	0.4599	4	0.4553	-1.0
acetone	ethanol	0.3472	298.1	0.5133	5	0.4860	-5.3

*References: 1, Aasen, et al. (1990); 2, Kumagai and Takahashi (1995); 3, Kouris and Panayiotou (1989); 4, Petrino, et al. (1995); 5, Wei, et al. (1985)

$$r_1 = 8 \times 0.6744 + 2 \times 0.9011 = 7.1974$$

$$r_2 = 42 \times 0.6744 + 2 \times 0.9011 = 30.127$$

$$q_1 = 8 \times 0.54 + 2 \times 0.848 = 6.016$$

$$q_2 = 42 \times 0.54 + 2 \times 0.848 = 24.376$$

Equations (9-13.8) and (9-13.9) give

$$\theta_1 = \frac{0.354 \times 6.016}{0.354 \times 6.016 + 0.646 \times 24.376} = 0.1191, \quad \theta_2 = 0.8809$$

$$\phi_1 = \frac{0.354 \times 7.1974}{0.354 \times 7.1974 + 0.646 \times 30.127} = 0.1158, \quad \phi_2 = 0.8842$$

Equation (9-13.7) is used to calculate the combinatorial contribution

$$\begin{aligned} \frac{\Delta^* g^{EC}}{RT} &= 0.354 \ln \frac{0.1158}{0.354} + 0.646 \ln \frac{0.8842}{0.646} + 5 \left[0.354 \times 6.016 \ln \frac{0.1191}{0.1158} \right. \\ &\quad \left. + 0.646 \times 24.376 \ln \frac{0.8809}{0.8842} \right] \\ &= 0.1880 \end{aligned}$$

In the mixture of groups, with CH_2 designated by subscript 1 and CH_3 by subscript 2:

$$\begin{aligned} X_1 &= \frac{8 \times 0.354 + 42 \times 0.646}{8 \times 0.354 + 42 \times 0.646 + 2 \times 0.354 + 2 \times 0.646} = 0.9374, \\ X_2 &= 0.0626 \end{aligned}$$

Equation (9-13.15) gives

$$\Theta_1 = \frac{0.9374 \times 0.54}{0.9374 \times 0.54 + 0.0626 \times 0.848} = 0.9051, \quad \Theta_2 = 0.0949$$

Equation (9-13.16) gives

$$\Psi_{12}^* = \exp\left(-\frac{66.53}{298}\right) = 0.7999, \quad \Psi_{21}^* = \exp\left(\frac{709.5}{298}\right) = 10.81$$

Equation (9-13.14) gives

$$\begin{aligned} \ln \gamma_1^* &= 0.54 \left[1 - \ln(0.9051 + 0.0949 \times 10.81) - \frac{0.9051}{0.9051 + 0.0949 \times 10.81} \right. \\ &\quad \left. - \frac{0.0949 \times 0.7999}{0.9051 \times 0.7999 + 0.0949} \right] \\ &= -0.1185 \end{aligned}$$

Similarly, $\ln \gamma_2^* = -3.3791$

In the mixture of groups from pure component 1, $X_1^{(1)} = 0.8$, and $X_2^{(1)} = 0.2$. Using Eq. (9-13.15) for pure component 1 then gives

$$\Theta_1^{(1)} = \frac{0.8 \times 0.54}{0.8 \times 0.54 + 0.2 \times 0.848} = 0.7181, \quad \Theta_2^{(1)} = 0.2819$$

$$\ln \gamma_1^{*(1)} = 0.54 \left[1 - \ln(0.7181 + 0.2819 \times 10.81) - \frac{0.7181}{0.7181 + 0.2819 \times 10.81} - \frac{0.2819 \times 0.7999}{0.7181 \times 0.7999 + 0.2819} \right]$$

$$= -0.4212$$

Similarly, $\gamma_2^{*(1)} = -1.0479$. In pure component 2, the results are $\Theta_1^{(2)} = 0.9304$, $\Theta_2^{(2)} = 0.0696$, $\ln \gamma_1^{*(2)} = -0.07655$, and $\ln \gamma_2^{*(2)} = -4.1201$. Equation (9-13.13) gives

$$\ln \gamma_1^{*R} = 8 \times (-0.1185 + 0.4212) + 2(-3.3791 + 1.0479) = -2.241$$

$$\ln \gamma_2^{*R} = 42(-0.1185 + 0.07655) + 2(-3.3791 + 4.1201) = -0.2799$$

Finally, the residual contribution is calculated with Eq. (9-13.12)

$$\frac{\Delta^* g^{ER}}{RT} = -(-0.354 \times 2.241 - 0.646 \times 0.2799) = 0.9741$$

Equation (9-13.6) is now used to calculate the mixture viscosity

$$\ln \eta_m = 0.354 \ln (0.2938) + 0.646 \ln (4.937) + 0.354 \ln (220) + 0.646 \ln (815.5) - \ln (604.7) - 0.1880 + 0.9741$$

$$\eta_m = 3.385 \text{ cP}$$

$$\text{Error} = \frac{3.385 - 3.278}{3.278} \times 100 = 3.26\%$$

Method of Teja and Rice (1981, 1981a)

Based on a corresponding-states treatment for mixture compressibility factors (Teja, 1980; Teja and Sandler, 1980) (See chap. 5), Teja and Rice proposed an analogous form for liquid mixture viscosity.

$$\ln(\eta_m \varepsilon_m) = \ln(\eta \varepsilon)^{(R1)} + [\ln(\eta \varepsilon)^{(R2)} - \ln(\eta \varepsilon)^{(R1)}] \frac{\omega_m - \omega^{(R1)}}{\omega^{(R2)} - \omega^{(R1)}} \quad (9-13.17)$$

where the superscripts (R1) and (R2) refer to two reference fluids. η is the viscosity, ω the acentric factor, and ε is a parameter similar to ξ in Eq. (9-4.15) but defined here as:

$$\varepsilon = \frac{V_c^{2/3}}{(T_c M)^{1/2}} \quad (9-13.18)$$

The variable of composition is introduced in four places: the definitions of ω_m , V_{cm} ,

T_{cm} , and M_m . The rules suggested by the authors to compute these mixture parameters are:

$$V_{cm} = \sum_i \sum_j x_i x_j V_{cij} \quad (9-13.19)$$

$$T_{cm} = \frac{\sum_i \sum_j x_i x_j T_{cij} V_{cij}}{V_{cm}} \quad (9-13.20)$$

$$M_m = \sum_i x_i M_i \quad (9-13.21)$$

$$\omega_m = \sum_i x_i \omega_i \quad (9-13.22)$$

$$V_{cij} = \frac{(V_{ci}^{1/3} + V_{cj}^{1/3})^3}{8} \quad (9-13.23)$$

$$T_{cij} V_{cij} = \psi_{ij} (T_{ci} T_{cj} V_{ci} V_{cj})^{1/2} \quad (9-13.24)$$

ψ_{ij} is an interaction parameter of order unity which must be found from experimental data.

It is important to note that, in the use of Eq. (9-13.17) for a given mixture at a specified temperature, the viscosity values for the two reference fluids $\eta^{(R1)}$ and $\eta^{(R2)}$ are to be obtained *not at T*, but at a temperature equal to $T[(T_c)^{(R1)}/T_{cm}]$ for (R1) and $T[(T_c)^{(R2)}/T_{cm}]$ for (R2). T_{cm} is given by Eq. (9-13.20).

Whereas the reference fluids (R1) and (R2) may be chosen as different from the actual components in the mixture, it is normally advantageous to select them from the principal components in the mixture. In fact, for a binary of 1 and 2, if (R1) is selected as component 1 and (R2) as component 2, then, by virtue of Eq. (9-13.22), Eq. (9-13.17) simplifies to

$$\ln(\eta_m \varepsilon_m) = x_1 \ln(\eta \varepsilon)_1 + x_2 \ln(\eta \varepsilon)_2 \quad (9-13.25)$$

but, as noted above, η_1 is to be evaluated at $T(T_{c1}/T_{cm})$ and η_2 at $T(T_{c2}/T_{cm})$.

Our further discussion of this method will be essentially limited to Eq. (9-13.25), since that is the form most often used for binary liquid mixtures and, by this choice, one is assured that the relation gives correct results when $x_1 = 0$ or 1.0. In addition, the assumption is made that the interaction parameter ψ_{ij} is not a function of temperature or composition.

The authors claim good results for many mixtures ranging from strictly nonpolar to highly polar aqueous-organic systems. For nonpolar mixtures, errors averaged about 1%. For nonpolar-polar and polar-polar mixtures, the average rose to about 2.5%, whereas for systems containing water, an average error of about 9% was reported.

In comparison with the Grunberg-Nissan correlation [Eq. (9-13.1)], with G_{ij} found by regressing data, Teja and Rice show that about the same accuracy is achieved for both methods for nonpolar-nonpolar and nonpolar-polar systems, but their technique was significantly more accurate for polar-polar mixtures, and particularly for aqueous solutions for which Grunberg and Nissan's form should not be used.

Example 9-23 Estimate the viscosity of a liquid mixture of water and 1,4-dioxane at 60°C when the mole fraction water is 0.83. For this very nonideal solution, Teja and Rice suggest an interaction parameter $\psi_{ij} = 1.37$. This value was determined by regressing data at 20°C.

solution From Appendix A, for water, $T_c = 647.14$ K, $V_c = 55.95$ cm³/mol, and $M = 18.02$; for 1,4-dioxane, $T_c = 587$ K, $V_c = 238$ cm³/mol, and $M = 88.11$. Let 1 be water and 2 be 1,4-dioxane. With Eq. (9-13.18), $\epsilon_1 = (55.95)^{2/3}/[(647.14)(18.02)]^{1/2} = 0.135$; $\epsilon_2 = 0.169$. From Eq. (9-13.19),

$$V_{cm} = (0.830)^2(55.95) + (0.170)^2(238) + (2)(0.830)(0.170) \times \frac{[(55.95)^{1/3} + (238)^{1/3}]^3}{8}$$

$$= 80.93 \text{ cm}^3/\text{mol}$$

and with Eq. (9-13.20),

$$T_{cm} = \{(0.830)^2(647.14)(55.95) + (0.170)^2(587)(238) + (2)(0.830)(0.170)(1.37) \\ [(647.14)(55.95)(587)(238)]^{1/2}\} / 81.29 = 697.9 \text{ K}$$

$$M_m = (0.830)(18.02) + (0.170)(88.11) = 29.94$$

So, with Eq. (9-13.18),

$$\epsilon_m = \frac{(80.93)^{2/3}}{[(697.9)(29.94)]^{1/2}} = 0.129$$

Next, we need to know the viscosity of water not at 333.2 K (60°C), but at a temperature of $(333.2)(647.14)/697.9 = 309.0$ K (35.8°C). This value is 0.712 cP (Irving, 1977a). [Note that, at 60°C, η (water) = 0.468 cP.] For 1,4-dioxane, the reference temperature is $(333.2)(587)/697.9 = 280.3$ K (7.1°C), and at that temperature, $\eta = 1.63$ cP (Irving, 1977a). Again this value is quite different from the viscosity of 1,4-dioxane at 60°C, which is 0.715 cP. Finally, with Eq. (9-13.25),

$$\ln[(\eta_m)(0.129)] = (0.830) \ln[(0.712)(0.135)] + (0.170) \ln[(1.63)(0.169)]$$

$$= -2.163$$

$$\eta_m = 0.891 \text{ cP}$$

The experimental viscosity is 0.89 cP.

Although the agreement between the experimental and estimated viscosity in Example 9-23 is excellent, in other composition ranges, higher errors occur. In Fig. 9-14, we have plotted the estimated and experimental values of the mixture viscosity over the entire range of composition. From a mole fraction water of about 0.8 (weight fraction = 0.45) to unity, the method provides an excellent fit to experimental results. At smaller concentrations of water, the technique overpredicts η_m . Still, for such a nonideal aqueous mixture, the general fit should be considered good.

Discussion

Three methods have been introduced to estimate the viscosity of liquid mixtures: the Grunberg-Nissan relation [Eq. (9-13.1)], the UNIFAC-VISCO method [Eq. (9-13.6)] and the Teja-Rice form [Eq. (9-13.24)]. The Grunberg-Nissan and Teja-Rice forms contain one adjustable parameter per binary pair in the mixture. The

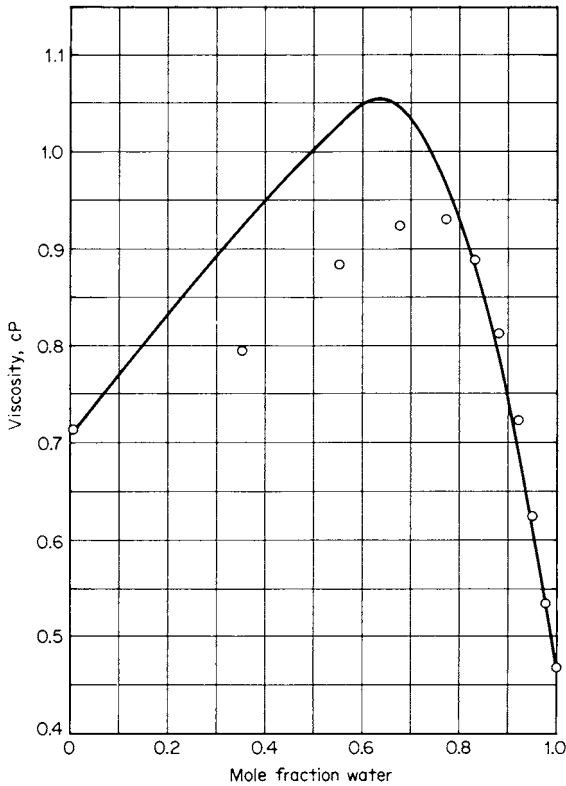


FIGURE 9-14 Viscosity of water and 1,4-dioxane at 333 K. Line is Eq. (9-13.25) with $\psi_{ij} = 1.37$; o experimental. (Irving, 1977a)

UNIFAC-VISCO method is predictive, but limited in the types of compounds to which it can be applied. The method correctly predicts the behavior of the methanol-toluene system which demonstrates both a maximum and minimum in the viscosity vs. concentration curve (Hammond, et al., 1958). An approximate technique is available to estimate the Grunberg-Nissan parameter G_{ij} as a function of temperature [Eq. (9-13.5)] for many types of systems. Teja and Rice suggest that their parameter ψ_{ij} is independent of temperature—at least over reasonable temperature ranges. This latter technique seems better for highly polar systems, especially if water is one of the components, and it has also been applied to undefined mixtures of coal liquids (Teja, et al., 1985; Thurner, 1984) with the introduction of reference components [See Eq. (9-13.16)]. The UNIFAC-VISCO method has been successfully applied to ternary and quaternary alkane mixtures (Chevalier, et al., 1988) but otherwise, evaluation of the above methods for multicomponent mixtures has been limited.

The above three methods are by no means a complete list of available methods. For example, Twu (1985, 1986) presents an equation to estimate the viscosity of petroleum fractions based on the specific gravity and boiling point. This method is

particularly useful for cases where the exact chemical composition of a mixture is unknown. Allan and Teja (1991) have also presented a method applicable to petroleum fractions and (Chhabra, 1992) presents a method for mixtures of hydrocarbons. Chhabra and Sridhar (1989) extend Eq. (9-11.6) to mixtures. For the treatment of electrolyte solutions, the reader is referred to Lencka, et al. (1998). Cao, et al. (1993) presented a UNIFAC-based method but our testing did not reproduce their excellent results in a number of cases. Other mixture correlations are reviewed in Monnery, et al. (1995) as well as the 4th edition of this book. For an example of gases dissolved in liquids under pressure, see Tilly, et al. (1994).

An equation developed by McAllister (1960) has been used successfully to correlate data for binary as well as multicomponent mixtures (Aminabhavi, et al., 1982; Aucejo, et al, 1995; Dizechi and Marschall, 1982a; Noda, et al., 1982). For binaries, the McAllister (1960) equation has been written to contain either two or three adjustable parameters. For ternary mixtures, the equation has been used with one (Dizechi and Marschall, 1982a) or three (Noda, et al., 1982) ternary parameters in addition to the binary parameters. Dizechi and Marschall (1982) have extended the equation to mixtures containing alcohols and water and Asfour, et al. (1991) have developed a method to estimate the parameters in the McAllister equation from pure component properties. Because of the variable number of parameters that can be introduced into the McAllister equation, it has had considerable success in the correlation of mixture viscosity behavior.

Lee, et al. (1999) used an equation of state method to successfully correlate the behavior of both binary and multicomponent mixtures. Nonaqueous mixtures required one parameter per binary while aqueous mixtures required two parameters per binary. One drawback of their method is the non-symmetrical mixing rule used for multicomponent aqueous mixtures (Michelsen and Kistenmacher, 1990). The equation of state structure allowed the method to be successfully applied to liquid mixtures at high pressure.

To finish this section, we again reiterate that the methods proposed should be limited to situations in which the reduced temperatures of the components comprising the mixture are less than about 0.7, although the exact temperature range of the Teja-Rice procedure is as yet undefined.

Should one desire the viscosity of liquid mixtures at high pressures and temperatures, it is possible to employ the Chung, et al. (1988) method described in Sec. 9-7 to estimate high-pressure gas mixture viscosities. This recommendation is tempered by the fact that such a procedure has been only slightly tested, and usually with rather simple systems where experimental data exist.

Recommendations to Estimate the Viscosities of Liquid Mixtures

To estimate low-temperature liquid mixture viscosities, either the Grunberg-Nissan equation [Eq. (9-13.1) or (9-13.2)], the UNIFAC-VISCO method [Eq. (9-13.6)] or the Teja-Rice relation [Eq. (9-13.17) or (9-13.25)] may be used. The Grunberg-Nissan and Teja-Rice methods require some experimental data to establish the value of an interaction parameter specific for each binary pair in the mixture. In the absence of experimental data, the UNIFAC-VISCO method is recommended if group interaction parameters are available. The UNIFAC-VISCO method is particularly recommended for mixtures in which the components vary greatly in size. It is possible to estimate the Grunberg-Nissan interaction parameter G_{ij} by a group contribution technique and this technique can be applied to more compounds than can the UNIFAC-VISCO method. All three methods are essentially interpolative in

nature, so viscosities of the pure components comprising the mixture must be known (or in the Teja-Rice procedure, one may instead use reference fluids of similar structure rather than the actual mixture components). The errors to be expected range from a few percent for nonpolar or slightly polar mixtures to 5 to 10% for polar mixtures. With aqueous solutions, neither the Grunberg-Nissan form nor the UNIFAC-VISCO method is recommended.

NOTATION

a^*	group contribution sum; Eq. (9-4.22)
b_o	excluded volume, $(2/3)\pi N_o \sigma^3$, Eq. (9-6.1)
C_v	heat capacity at constant volume, J/(mol·K); C_p , structural contribution in Eq. (9-4.22) and Table 9-3 C_{br} , number of carbon atoms in a branch
D	diffusion coefficient, cm^2/s or m^2/s
F_c	shape and polarity factor in Eq. (9-4.11); F_p^o , low-pressure polar correction factor in Eq. (9-4.18); F_Q^o , low-pressure quantum correction factor in Eq. (9-4.19); F_p , high-pressure polar correction factor in Eq. (9-6.10); F_Q , high-pressure quantum correction factor in Eq. (9-6.11)
g_{ij}	radial distribution function, Eq. (9-7.14)
G_1, G_2	parameters in Eqs. (9-6.21) and (9-6.22); G_{ij} parameter in Eq. (9-13.1)
Δ^*g^{EC}	combinatorial contribution to viscosity in Eq. (9-13.6)
Δ^*g^{ER}	residual contribution to viscosity in Eq. (9-13.6)
k	Boltzmann's constant
L	mean free path
m	mass of molecule
M	molecular weight
n	number density of molecules; number of components in a mixture
N	number of carbon atoms or parameter in Eq. (9-11.2); ΔN , structural contribution in Eq. (9-11.5) and Table 9-10; N_o , Avogadro's number
P	pressure, N/m ² or bar (unless otherwise specified); P_c , critical pressure; P_r , reduced pressure, P/P_c ; P_{vp} , vapor pressure; $\Delta P_r = (P - P_{vp})/P_c$
q_i	surface area parameter for molecule i
Q	polar parameter in Eq. (9-6.5); Q_k , surface area parameter of group k
r	distance of separation; r_i , volume of molecule i
R	gas constant, usually 8.314 J/(mol · K), R_η , parameter in Eq. (9-6.4); R_k , volume parameter of group k
T^*	kT/ε
T	temperature, K; T_c , critical temperature; T_r , reduced temperature, T/T_c ; T_b , boiling point temperature; T_{fp} , melting point temperature
v	molecular velocity
V	volume, cm^3/mol ; V_c , critical volume; V_r , reduced volume, V/V_c , or in Eq. (9-6.3), V/V_o ; V_o , hard packed volume used in Eq. (9-6.3) or parameter in Eq. (9-11.6)
x	mole fraction, liquid
y	mole fraction, vapor; parameter in Eq. (9-6.20)

- Y parameter in Eq. (9-6.9)
 Z compressibility factor; Z_c , critical compressibility factor; Z_1 , Z_2 , parameters in Eqs. (9-6.6) to (9-6.8)

Greek

- γ orientation factor in the Brulé-Starling method, Table 9-8, or obtain from Brulé-Starling (1984)
 Δ correction term in Eq. (9-6.17)
 ε energy-potential parameter; variable defined in Eq. (9-13.18)
 η viscosity (usually in micropoises for gas and in centipoises for liquids); η^o , denotes value at low-pressure (about 1 bar); η_c , at the critical point; η_c^o , at the critical temperature but at about 1 bar; η^* , η^{**} , parameters in Eqs. (9-6.19) and (9-6.23), η_r , reduced viscosity, defined in either Eq. (9-4.13) or (9-6.4), η_b , at the normal boiling point temperature
 θ_i , Θ_k surface area fraction of molecule i or group k
 κ polar correction factor in Eq. (9-4.11), see Table 9-1
 λ thermal conductivity, W/(m · K)
 μ dipole moment, debyes; μ_r , dimensionless dipole moment defined in either Eq. (9-4.12) or Eq. (9-4.17)
 ν kinematic viscosity, η/ρ , m²/s
 ξ inverse viscosity, defined in Eq. (9-4.14) or Eq. (9-4.15); ξ_r , inverse viscosity defined in Eq. (9-6.13)
 ϕ_i volume fraction of molecule i
 ρ density (usually mol/cm³); ρ_c critical density; ρ_r , reduced density, ρ/ρ_c
 σ molecular diameter, Å
 ψ intermolecular potential energy as a function of r
 Ψ radial distribution function
 ψ_{ij} interaction parameter in Eq. (9-13.24)
 ω acentric factor, Sec. 2-3
 Ω_v collision integral for viscosity

Subscripts

- i, j, k components i, j, k
 $1, 2$ components 1, 2
 L liquid
 m mixture
 SL saturated liquid

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